Flushability of Nonwoven Wet Wipes

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The candidate confirms that the work submitted is his/her own and that appropriate credit has been given where reference has been made to the work of others.

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Abstract

Particular hygiene applications, such as Moist Toilet Tissue (MTT), toddler wipes, bathroom cleaning wipes and feminine hygiene wipes lend themselves to convenient disposal via the sewer network. The high volume of wipes now disposed of through the sewer network is increasing pressure on pipework systems and wastewater treatment plants. The main objectives of this study were to review the prior art and published literature on flushable nonwoven technology, identifying the fundamental mechanisms of function, benchmark the performance of currently available commercial flushable wipes and through experimentation and empirical modeling, begin to form an understanding of flushable wet wipe structure-property relationships. Commercially available wet wipes were found to exhibit varying dispersibilities when assessed using the industry-standard shake-flask test methodology, a test designed to assess the disintegration of a wipe following disposal in the sewer network. All were composed from cellulose, usually blends of wood pulp and lyocell. It was observed that fibrillation of lyocell increased as a result of mechanical agitation during dispersibility testing. These fibrils apparently hindered the dispersion of the wipe into individual fibres. In experimental wipes, fibre fibrillation was found to have a negative influence on the dispersibility behaviour of both wetlaid and airlaid hydroentangled wipes. Hydroentangled fabrics containing non-fibrillating regenerated cellulose fibres exhibited the greatest resistance to fibrillation and also the highest dispersibility. Experiments were performed to assess the wet strength and dispersibility of both wetlaid and airlaid hydroentangled wipes composed of

wood pulp and regenerated cellulose. The influence of fabric structure including fibre length, aspect ratio (fineness), blend composition and process (specific energy and hydroentanglement forming belt open area) were studied. Based on the findings from the present work, using an airlaid-hydroentangled platform it is possible to produce a wet wipe with a wet strength as high as 22 N/50mm with dispersibility of 100% (<12.5 mm screen), which exceeds the aspirational target of 15 N/50 mm and ≥95% dispersibility (12.5 mm screen). Empirical models based on linear multiple regression methods suggested specific energy and the total regenerated fibre length positively influence the wet tensile strength of the fabrics. However, the total fibre length negatively influences dispersibility. Fibres that are resistant to fibrillation were found to benefit dispersibility. The model for wet tensile strength was found to have a relatively good correlation with the experimental data, but less so for dispersibility. Furthermore, it was established that the most likely dispersion mechanism in the shake flask is the result of fibre slippage, meaning that wet fibre-to-fibre cohesion and frictional resistance to sliding is critical in governing the break-up of the substrate. To understand the magnitude of the wet cohesive forces involved, a wet pull out test was devised. Airlaid-hydroentangled wipes with a carboxymethylcellulose (CMC) binder exhibited improved dispersibility performance but with decreased wet tensile strength. This could be explained in terms of the modification of the coefficient of friction by the CMC allowing the fibres to separate more easily when subjected to mechanical forces during agitation. Optimum pH conditions and electrolyte addition levels were established for the stabilisation of CMC binder in wet-wipes.

Contents

List of Tables

List of Figures

List of Abbreviations

WwTWs	Wastewater treatment works
CMC	Carboxymethyl Cellulose
CTMP	Chemi-Thermo-Mechanical Fluff Pulp
MTT	Moist Toilet Tissue
ATR-FTIR	Attenuated Total Reflectance-Fourier Transform Infra Red Spectroscopy
XMT	X-Ray Microtomography
CAT	Computed Axial Tomography
SEM	Scanning Electron Microscopy
CSF	Candian Standard Freeness
EDANA	Organisation representing the European nonwovens industry
INDA	Organisation representing the USA nonwovens industry
WSP	World Strategic Partners (collaboration of INDA and EDANA)
CSO	Combined Sewer Overflow
CAGR	Compound Annual Growth Rate
MD	Machine Direction
CD	Cross Direction
WBL	Mean Wet Breaking Load
FIB	Fibrillation
TFL	Total Fibre Length
SE	Specific Energy
ANOVA	Analysis of Variance
TAHT	Triacrylamido-Trihydrotriazine

w/v	weight per volume
w/w	weight per weight
D.S.	Degree of Substitution
WERF	Water Environment Research Foundation
PVA	Polyvinyl Alcohol
WRc	Water Research Centre
Dtex	Decitex
GD3	Third Edition of the WSP Flushability Guidelines
FMCG	Fast Moving Consumer Goods

Chapter 1
Introduction

1.1 Growth of Wipes and the Impact on the Sewer System

The impact of the sewer network on public health is considerable. In the USA and Europe, improvements during the nineteenth century helped to combat waterborne diseases such as cholera, diarrhoea, typhoid and dysentery. During that time in major cities, nearly half of the total reduction in mortality, three quarters of infant mortality, and nearly two thirds of child mortality were attributed to the availability of clean water (1). Improvements in sanitary conditions, attributed to the provision of sewers and waterworks, have been estimated to have reduced overall mortality rates in the UK by as much as 25% (2, 3).

The disposal of products via the sewer network has long been perceived as a highly convenient, hygienic method of disposing soiled paper. Whilst toilet tissue has been sold in consumer-friendly forms since the nineteenth century (4), the sewer system is able to cope with large volumes due to its rapid dispersibility in water, short fibre construction and extremely high cellulose content, such that it is inherently biodegradable.

Pre-moistened wipes, wet wipes and moistened towelette are terms used to describe lightweight, single use, nonwoven fabrics impregnated with an aqueous medium for the purposes of cleaning. Such products are immediately disposed of after use. From their initial application in baby wipes, the market has grown substantially and is highly segmented, including a multitude of applications in the personal care, industrial, healthcare and medical areas. Much of the growth in pre-moistened wipe consumption occurred after 1990 where the barriers to market entry were overcome by improvements in manufacturing technology.

Global production of wet wipes has increased rapidly since their inception during the 1970s. The industry witnessed compound growth of over 10% per annum throughout the late 1990s and early 2000's and volume growth of over 3.65% Compound Annual Growth Rate (CAGR) is predicted up to 2019 (5). The growth has been driven by consumer demand for increased convenience, increasing affluence, ageing populations, a desire for hygienic disposal and an increase in the relative affordability of wipe products. The continued sales growth in nonwoven wipes from 1997-2015 is highlighted in Figure 1.1 (6).

The growth has continued despite signs that the global wipes market is being affected by increasing consumer price sensitivity (7).

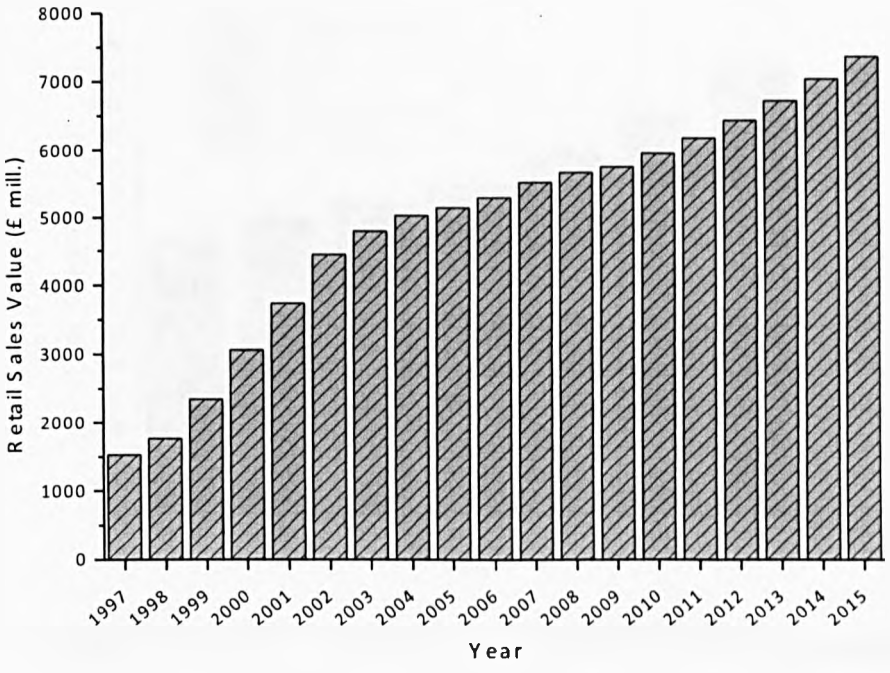


Figure 1.1. Global Wipes Market, Retail Sales 1997–2015 (£ million) (6)

Certain applications for wipes, such as adult Moist Toilet Tissue (MTT), toddler toilet care wipes, bathroom cleaning wipes, incontinence/bathing wipes and feminine hygiene wipes lend themselves to convenient disposal via the sewer network because they are likely to be contaminated with human body fluids or waste during use. These applications have driven the development of "flushable" nonwoven wet-wipes by a number of manufacturers in which consumers are actively encouraged to use the sewer system disposal for reasons of convenience and hygiene. Production of flushable wipes by volume has therefore increased and was predicted to represent up to 7.3% of the total volume of wipes sold in 2013 (8). Growth in the global sales value of flushable wipes by manufacturer are summarised in Figure 1.2. Sales are expected to increase rapidly at 12.1% annually from 2015-2016 as new capacity is commissioned in Spain, Israel, Turkey and China (9-12).

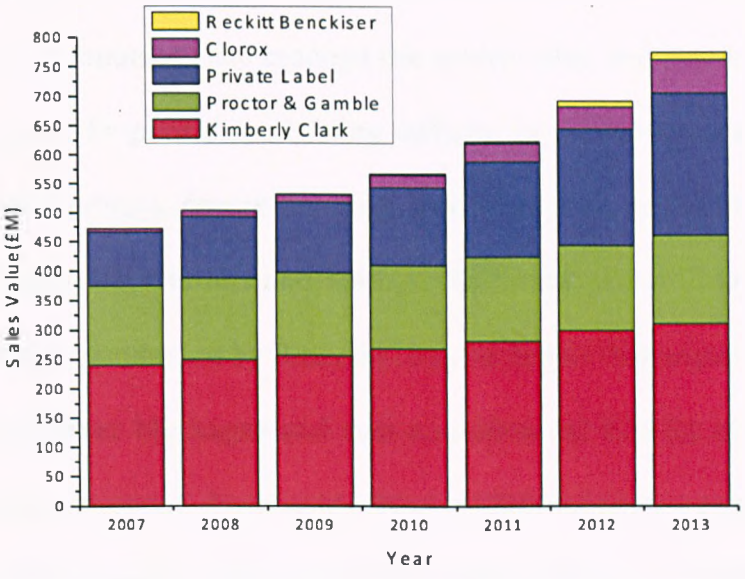


Figure 1.2. Global Sales of Flushable Wipes 2007-2013 (£ million), adapted from Mango (8)

Not surprisingly, growth in the sales of flushable wipes has resulted in an increased volume of wipes being disposed of in toilets across the developed world increasing the demands on existing municipal sewer networks. Whilst this has mostly affected developed countries within Europe, Japan and the USA, sales volumes have increased at more than 18% annually in the emerging markets of Asia and South America (8) raising concerns that too much demand may be being placed on sewer networks.

The water industry has been increasingly concerned about the impact of flushable wipes and has published strongly worded policies regarding the disposal of wipes and related products (13). Essentially, the concern relates to the fact that wipes described as flushable do not break up and disperse as effectively as conventional toilet tissue when disposed of in the toilet, such that describing these products as 'flushable' is misleading. The issue has highlighted

the poor design of many wipes products, which have created major problems for the water companies who manage the wastewater and sewer systems. The problems caused by poor dispersibility include, an increasing number of sewer blockages, foul odours, sewer flooding, environmental pollution and adverse impacts on pumping stations and sewage treatment plants (14). One study in the Netherlands, conducted by Rioned (15), concluded that wipes contribute up to 60% of all sewer blockages and cost an additional €26-51 million in pump repairs and replacement, drain unblocking, additional energy consumption and environmental damage. Consequently, the water industry developed its own highly challenging protocols for assessing the performance of flushable materials, initially without consultation with the product producers (13, 14, 16, 17).

Wastewater Treatment Works (WwTWs) generally consist of three treatment processes. The preliminary or primary sewage treatment involves removing larger debris from the wastewater by settlement and screening. Secondary sewage treatment involves biological decomposition of the waste using aerobic bacteria usually via a trickling filter bed or the activated sludge process (18). Finally, a tertiary treatment to separate the solids from the treated effluent is conducted where the treated effluent is returned to watercourses whilst the solids are collected and either burnt (after drying) or sold.

The UK water research company, WRc Plc., has identified a number of problems caused by wipes that do not disintegrate on disposal (19), including:

- Snagging on drainlines and in sewers creating blockages,

- During heavy rainfall, wipes may be discharged into the natural environment via Combined Sewer Overflows (CSOs),
- Increasing the volume of solids being collected on screens at wastewater treatment works (WwTW), which are disposed to landfill,
- Snagging on WwTW screens, inhibiting the cleaning mechanism.

Figure 1.3 illustrates some of the issues observed at the screens in WwTWs. Screens at WwTWs are designed with 5-6 mm openings, such that any sewer solids greater than 6 mm are likely to be retained on the screens and be treated as municipal solid waste or be utilised as an inefficient feedstock for energy recovery via incineration (18).

(a) Fibrous materials on screens at WwTW (b) Fibrous materials removed using WwTW screens

Figure 1.3. Problems associated with fibrous materials on screens at WwTWs (18)

It is critical that flushable wipes be fully biodegradable and water dispersible and that any particulates can be removed in the activated sludge and be recycled as an agricultural biosolid (18).

Today, although there is an improved understanding of the concerns of the water industry there is a still a performance gap in terms of the availability of wipes with satisfactory water dispersibility characteristics. One of the main problems for the nonwoven wipe producers is the complexity of disposal routes via sewer networks. Also, the design of sewer networks can vary substantially even within the same country. Figure 1.4 shows some of the most common disposal routes.

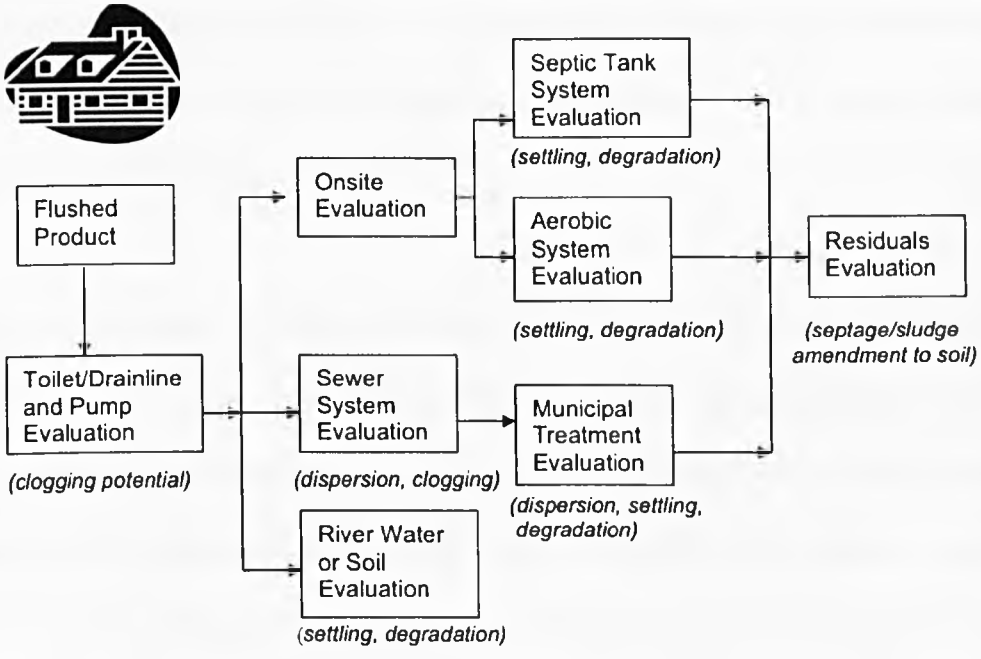


Figure 1.4 Disposal routes for flushable wipes (20, 21)

After disposal, the wipes must clear the building's toilet and drainline system, be transported in wastewater conveyance systems and be compatible with wastewater treatment or alternatively untreated discharges of untreated wastewater (21). This coupled with the fact that few WwTWs are of the same design means that some service large cities whilst small rural WwTWs can service as few as 100 inhabitants (18). There is also evidence that the trend towards improving water conservation by reducing toilet flush volumes (<6 L)

will result in increasing problems with wipes since there could be insufficient water to facilitate their rapid dispersal at the time of flushing (22).

The issue of sewer disposal of wipes is also a subject of political interest in the USA and Europe. In 2010, the Huffman bill (23) to ban flushable wipes was defeated in California (USA), but almost immediately another was tabled in New Jersey (USA) (24, 25). Recently, wet wipe manufacturers have been forced by government regulators to remove flushable claims which are not substantiated (26). In 2015 the city of Wyoming in the USA filed a federal class action lawsuit against six manufacturers of wet wipes, due to flushable wipes clogging the city's sewer network (27).

With increasing pressure upon the nonwoven producers to act responsibly, the industry has sought to improve products by developing protocols for the assessment of flushable product performance. The WERF (Water Environment Research Foundation) protocols (28), released in 2003, were the first attempt to assess the flushability of wipes. Subsequently, the nonwoven trade associations in North America (INDA) and Europe (EDANA) have made concerted and combined efforts to improve the WERF protocols by developing industry guidelines, culminating in the INDA and *EDANA Flushability* Testing *Guidelines* (20, 21, 29). Note that these are only voluntary guidelines and not formal standards, but they are intended to improve the performance and labelling of flushable and non-flushable wipes. The issue of flushable versus non-flushable products is a contentious one. There is evidence to suggest that many items that are flushed in the toilet are not designed to be flushable (30) and were never intended to be flushed by their manufacturers. This includes

products such as cotton buds, kitchen towels and non-flushable baby wipes. An INDA study in 2010 suggested that the majority of wipes blocking the system were constructed from long fibres (>20 mm), and were never designed or intended to be flushed (31, 32). The general view from industry is that improvements in flushable wipe technology should be accompanied by strategic marketing and improved labelling to ensure consumers are properly informed about appropriate disposal methods.

1.2 Definition and development of flushable nonwovens

Whilst the performance requirements for flushable wet-wipes are contradictory, i.e. high wet strength during use but low wet strength on disposal, manufacturers have used different approaches to solve the problem. Until the release of the World Strategic Partners (WSP) *Flushability* Testing *Guidelines* in 2008 there was no consistent or widely accepted definition of what constitutes a 'flushable' nonwoven product. According to industry guidelines, flushable products are those that (21):

- Clear toilets and properly maintained drainage pipe systems under expected product usage conditions,
- Are compatible with existing wastewater conveyance, treatment, reuse and disposal systems,
- Become unrecognisable in a reasonable period of time and be safe in the natural receiving environments.

This definition of a flushable product provides little in the way of measurable properties and highlights the need for further research aimed at developing a

set of standards that can be agreed between the wipe manufacturers and the water industry.

The performance of flushable fibre-based products has improved since their inception as indicated in Figure 1.5. Early patents for flushable products first appeared during the 1930's and focused upon products that were dry during use but disintegrated or were partially solvated in aqueous environments (Dry-to-Aqueous) (33). Prior to the 1960's, the fabrics incorporated naturally occurring binder substances such as gelatine, gum arabic, vegetable gums, methylcellulose, ethylcellulose, soluble starches and dextrin (33-37). After the introduction of water-soluble polyvinyl alcohol (PVA) during the 1960's, synthetic polymers gained ground in dry-to-aqueous flushable product applications (37-45) at the expense of the naturally occurring polymers.

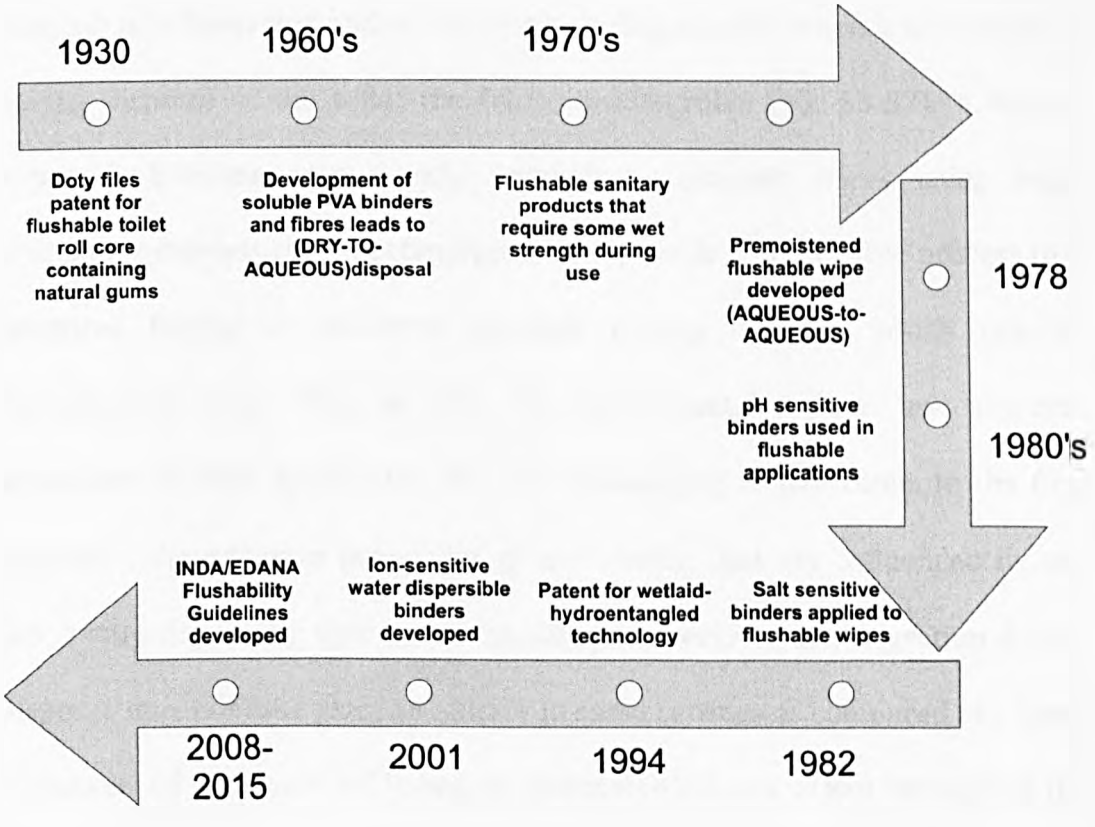


Figure 1.5. Timeline for the development of flushable products

During the 1970's, the sanitary industry started to develop flushable nonwoven products and applications in feminine hygiene, baby's nappies (diapers) and wipes were targeted (37, 38, 42, 46-52). These products required the constituent fabrics to have sufficient wet strength when insulted with bodily fluids but yet ideally required complete disintegration when disposed of in the toilet. Technically, this was extremely challenging.

During the 1980's to date, flushable wet-wipe technology was developed that enabled products to be made with higher wet strength during use but which more effectively disintegrated in large volumes of water (Aqueous to Aqueous). Whilst various approaches have been adopted over the years, today, two main approaches are now in commercial use. The first approach involves using the lotion that is applied to the fabric during manufacture to enhance tensile strength of adhesively bonded substrates during use, but when it is washed off during disposal in the toilet the fabric disintegrates (43, 53-57). A second approach involves mechanically entangling cellulosic fibres using high-pressure water-jets (hydroentanglement) to provide a binder-free process that produces fabrics of sufficient strength during use but which can be disintegrated after disposal (58, 59). Unfortunately, there are practical limitations in both approaches that are challenging to overcome. In the first approach, the adhesive properties of the binder, that are influenced by the lotion vary depending upon water quality and therefore disintegration during disposal, may not take place as quickly in some settings as compared to others. In the second approach, achieving an acceptable balance of wet strength in the fabric and dispersibility in the toilet remains challenging.

The most challenging unmet need for flushable nonwovens is in the engineering of pre-moistened or wet-wipe substrates because of the counter-intuitive requirements of high wet strength during use and very low wet strength leading to disintegration, immediately on disposal. Accordingly, the focus of this thesis is centred on substrate development for nonwoven wet wipes. Given the challenges of balancing such divergent technical requirements regarding wet strength and disintegration, research is required to develop understanding of how fabric composition and properties can influence both.

It is evident that state of the art technology for producing dispersible nonwoven substrates necessitates the use of wood pulp and/or short-cut fibre to aid dispersion, and to ensure cost-effectiveness a blend of the two components is required. Furthermore, hydroentanglement has become a preferred method of bonding in the manufacturing route. Based on blends of wood pulp with short-cut cellulosic fibres, the overall aim of this research was to study the effects of blend composition, fibre properties and manufacturing conditions on the structure and properties of hydroentangled wet-wipe substrates. Such a study was considered necessary in order to identify the most appropriate conditions needed to balance the essential pre-requisites of a functional substrate, i.e. high wet strength (after lotion is applied to the fabric) and dispersibility during disposal.

The specific objectives were:

- To critically review current dispersibility technology and the functional requirements of nonwoven wet-wipe substrates.
- To understand the wet strength and dispersibility behaviour of existing commercially-available nonwoven substrates, claimed to be 'flushable'.
- To study the influence of fibre composition and dimensions, as well as process conditions on the balance of wet strength and dispersibility developed in nonwoven substrates.
- To identify the key factors governing wet strength and dispersibility and establishing a method of preparing fabrics with an improved balance of these properties, as compared to existing, currently available wipe substrates.

Chapter 2

Review of Literature

2.1 Introduction

This chapter details the approaches that have been attempted for engineering wipe substrates with the combined requirements of high wet strength during use and rapid dispersibility during disposal in the toilet. In practice, this particular combination of properties is extremely challenging to achieve. During manufacture, wet wipes are typically loaded with 100-600% w/w (53, 60) of aqueous lotion and the substrate must remain sufficiently strong to be processed, packaged, stored and then used by the consumer without disintegrating. Then, preferably immediately on disposal in the toilet, the substrate should disintegrate such that the particle sizes are sufficiently small not to foul pipework, pumps or screens during transit to the sewage processing plant. Accordingly, identifying methods of producing sufficiently high wet strength is key to the design of a functional substrate.

2.2 Test protocols to assess flushability

The establishment of test protocols to assess flushability provides some insight of the requirements for a flushable wipe. An understanding of the testing criteria can help to inform wipe substrate design and improve compatibility of the product with wastewater systems. The available test protocols are

reviewed here to understand the performance requirements for flushable wipes.

Attempts have been made to establish test methods and protocols, which aim to simulate the behaviour of flushable products within the sewer system. For many years, no official guidelines to measure flushability were available leading to companies designing their own test methodology. The WERF protocols (28), released in 2003 were the first attempt to provide a uniform approach in assessing and quantitatively measuring the flushability of wipes. Subsequently, the associations of INDA and EDANA World Strategic Partners (WSP) have sought to improve the WERF protocols with combined industry guidelines culminating in the WSP Flushability Guidelines in 2008. These were updated in 2009 and a third edition published in 2013 (20, 21, 29). These guidelines focus on the USA and Europe to rectify some of the issues arising from flushable products (20, 21, 28).

The water industry established its own protocols in isolation from the nonwoven producers as well as stringent policies regarding flushable products (13, 14, 16, 17). The water industry's guideline, Test Protocol to Determine the Flushability of Disposable Products (2008) was developed by the Water Research Centre (WRc), a UK water research company. Despite ongoing efforts of the nonwoven and wastewater industry, no collective standard for assessing flushable products has been agreed to date. The guidelines currently available are biased as their development is driven by the particular trade association but helps to inform the requirements for flushability.

A common goal of both industries is to establish a protocol that allows the accurate assessment of product's behaviour after disposal down the toilet. Accordingly, some similarities in the underlying principles applied in their guidelines can be found. Figure 2.1 shows the disposal routes that should be considered when developing test protocols for flushable materials.

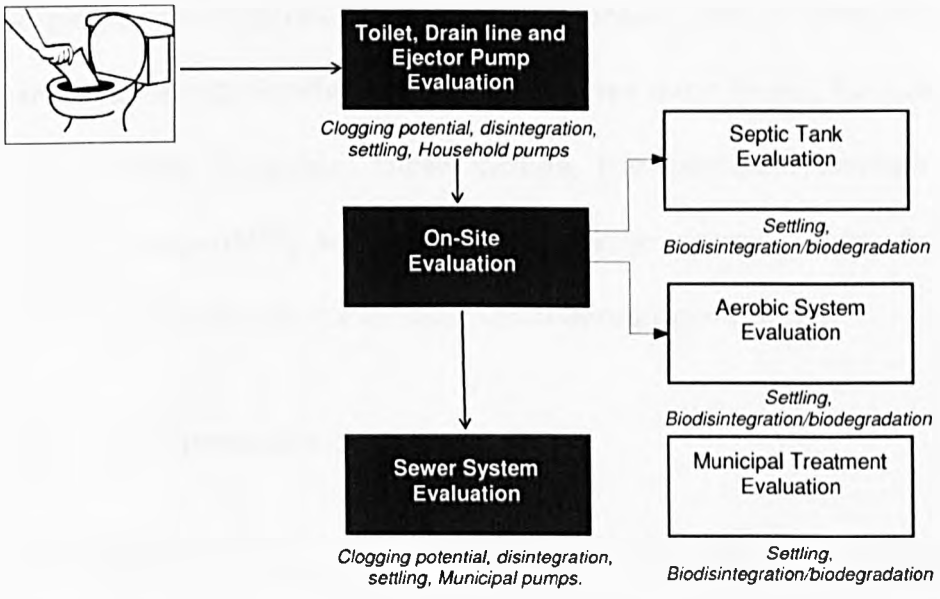


Figure 2.1. Disposal routes for products flushed down the toilet (29)

From Figure 2.1 it can be observed that all flushable products must pass through the toilet, drain line and ejector pump. Once the initial household system has been cleared there are two potential disposal routes depending upon the treatment system employed; on-site treatment or municipal sewer and wastewater treatment. The requirements for each route are different, for a product to be considered flushable it should be compatible with both type of system. Additionally, across the world the routes of wastewater disposal vary, starting with diverse toilet designs and drains through to different disposal systems including municipal wastewater collection and treatment, onsite wastewater treatment (septic tank system), or untreated discharge; a fact,

which further complicates the establishment of uniform standards. For example, the Netherlands has a large amount of pumps, due to the lowland nature of the terrain (17), therefore any flushable wipe should pass through a foul pump without blocking or causing an excessive increase in energy use.

Despite the diversity of conditions after disposal however, there are several key performance criteria which all protocols agree must be met for a nonwoven to be considered flushable. These include, transportation through pipework, settling, compatibility with household sewage ejector pumps, disintegration and biodegradation under aerobic and anaerobic conditions.

2.2.1 Transportation

The ability of a wipe to be transported from the toilet, via the household drain and private sewer system to the main public sewer system or septic tank is critical to prevent blockages. In drains and small sewers the flows tend to be low volume and intermittent, the wipe must be capable of being propelled by these flows. The test systems consist of a toilet and drain line, which should be cleared by the wipe in a specified number of flushes.

2.2.2 Settling

The buoyancy of a wipe will determine whether the material will sink (settle) in wastewater. Settling points include sumps, septic tanks, onsite aerobic systems and settling chambers that are associated with pump stations and municipal wastewater treatment plants (29). Settling is important behaviour to

ensure that the product will settle in a household sewage ejector pump basin. If a product does not settle, it may cause blockage of the inlet pipe or interfere with pump controllers. Test protocols measure the sinking of a wipe through vertical pipe filled with water. The wipes should settle within a 24 hours period.

2.2.3 Compatibility with household sewage ejector pumps

Compatibility with household sewage ejector pumps is necessary to prevent blockages within the household pipework. A sewage ejector pump is commonly installed when a bathroom is situated below the elevation of a main sewer or septic tank. The pump is used to pump liquids and solids up into the main sewer or septic tank pipework. Passage through such a system ensures that the product does not clog, accumulate within or interfere with switching device that activates the pump. The test protocol includes operating a household sewage ejector pump assembly, consisting of a basin and submersible pump, which is fed from a toilet and drainline. Wipes are loaded into the system at a specified rate over a set period of time. To pass the test the product must not cause the system to stop functioning and an excessive build up of wipes in the system prevented. Settling is a prerequisite to this test otherwise the wipe would not enter the submersed pump.

2.2.4 Disintegration

All test protocols agree that flushable products should break up, as toilet paper does, into smaller particles to make them compatible with sewer disposal.

Screening occurs at the inlet of wastewater treatment works or the outlet of combined sewer overflows (CSOs), these screens commonly have aperture sizes of 6 mm square. The tests are designed to assess the potential for a product to disintegrate when subjected to mechanical agitation in water or wastewater. The mechanical action simulates the vigorous turbulence experienced at a pumping station. There are several tests designed to simulate the turbulent water flows; the shake flask, tipping tube or slosh box (14, 21, 29). The tests create conditions of turbulent flow by rotation or reciprocating translational motion of a vessel containing water and a wipe for a set period of time. The disintegration of the wipe is measured by rinsing the residual fibre through a number of apertured screens and weighing the wipe mass captured by each screen size.

2.2.5 Passage through a municipal sewer pump

Municipal Sewer Pumps are used in a sewer lift station or within a wastewater treatment plant to move wastewater. Blockages of pumps caused by wipes have been identified as a major concern (13, 15, 61). The passing of wipes can increase energy consumption of sewer pumps and pumping stations as pumps have an optimum number of revolutions at which they pump wastewater efficiently. As a pump becomes blocked by wipes or other materials, it starts to function uneconomically and may be stopped completely by a build-up of wipes and other materials. The testing involves introducing wipes every 10 seconds for 10 minutes into an operating municipal pump whilst monitoring power

consumption. The average power increase over the baseline should not exceed 15%.

2.2.6 Aerobic and anaerobic biodisintegration/biodegradation

The majority of wastewater treatment processes end in a biodegradation process. To be fully compatible with these processes a wipe must be capable of being biodegraded/biodisintegrated aerobically and anaerobically by microorganisms. To be subjected to these processes the wipes should comply with all the other performance criteria, otherwise it is unlikely to reach the biodegradation/biodisintegration process, e.g., if the wipe is not dispersible then it will be captured on the screens and not enter the wastewater treatment works.

Aerobic biodegradation processes are employed in municipal biological wastewater treatment, aerobic sludge digestion, aerobic onsite wastewater treatment, aerobic soils and aerobic aquatic environments. To test aerobic biodisintegration, the total mass of a product retained on a 1 mm screen after being incubated with activated sludge for 14 days at ambient laboratory temperature is measured. Over 95% of the mass should pass through the screen. Biodegradation is measured by measuring the evolution of CO_2 resulting from the mineralisation of the organic material in the product, the amount of carbon dioxide must exceed 60% after 28 days.

Anaerobic biodisintegration/biodegradation processes are employed in anaerobic digesters, septic tanks and surface water sediments. The criteria for anaerobic biodisintegration are met when >95% of the mass of a wipe pass through a 1 mm screen after being incubated in anaerobic sludge for 28 days at 35±2°C. Anaerobic biodegradation conditions are met when the evolution of gas (carbon dioxide and methane) resulting from the mineralisation of the organic material exceeds 70% after 56 days.

2.3 Performance criteria for flushable wipes

The test methods described in section 2.2 inform us of the performance criteria required of a flushable wipe. It can be observed that clearance of the toilet and immediate pipework into the main sewer alone does not confer flushability. One of the earliest commercial ways of imparting flushability was to reduce the dimensions of pre-moistened wipes by over 50% (62). This may prevent immediate clogging of domestic drainage systems and enable conveyance through to wastewater treatment facilities but fails to address many of the other performance requirements.

Reducing the size of the wipe alone does not address the disintegration (dispersion) of the product on entering the sewer network, transportation, buoyancy, biodegradability and compatibility with wastewater treatment processes. As wet wipe sales have increased in the developed world, disruption of wastewater systems have become a major concern to the water authorities

(13, 61, 63-65) because the wipes being sold do not meet flushable performance requirements.

To be transported through pipework or to settle in a septic tank the wipe's buoyancy must be considered. The product should not float on wastewater and should preferable be constructed mainly from materials with a density greater than 1000 $kg.m^{-3}$. At the same time the constituent materials should not be so dense as to prevent pick-up and transfer by the intermittent, relatively low flows found in drains and small sewers. The mechanism of wipes causing pump clogs is not well understood. One study found that 70% of the wipes causing the pump clogs were personal and cleaning wipes (66) that were not designed to be dispersible or flushable. The wipes were constructed from long staple fibres (>30 mm) (31). Flushable wipes should also be composed from aerobically and anaerobically biodegradable raw materials. Cellulose is the only material that is proven in the application as it is the main constituent of toilet paper, which is considered a flushable material. Cellulose accounts for over 75% by weight of the fibres used in flushable wipes (8).

Understanding the difference between the terms flushable and dispersible is essential to understand the approaches that have been adopted to engineer wipes that are more compatible with the toilet and wastewater system. Whilst dispersibility is a critical performance requirement, it is only one parameter, which alone does not guarantee flushability. All the performance criteria should be met for a wipe to be considered truly flushable. Technically, the main challenge is the development of water dispersible substrates, since this will

inevitably lead to improved flushability and compatibility with wastewater systems. In addition to adequate wet tensile strength, dispersibility in water on disposal of the wipe is critical for product acceptance. Unfortunately, the wet tensile strength of the nonwoven substrate is usually compromised to impart dispersibility.

2.4 Formation of flushable wipe substrates

Fabric formation processes employed in the manufacture dispersible wipes include all the main methods of web formation (drylaid, wetlaid and spunmelt) and bonding (thermal, mechanical and chemical). Principally airlaid and wetlaid processes are preferred as they produce webs from short (<20 mm) fibres; practically fibres between 2-15 mm are preferred (67). A detailed description of these processes is provided in Chapter 3 and some of the common commercially available nonwovens are analysed in Chapter 4. The short fibres used in these processes are believed to give rise to improved dispersion because of the relative ease by which the fibre assembly can be disintegrated in a hydrodynamic environment compared to longer fibres (58, 68). For this reason, carding processes, which require longer fibre lengths (>15 mm) play a minor role in the manufacture of substrates for pre-moistened flushable wipes (8).

The majority of the literature on water dispersible and flushable wipe technology is in the patent literature detailing the results of work carried out by commercial developers and there are few academic studies. A study by Lang

(69) grouped the primary mechanisms that have been exploited for the manufacture of flushable wipes in to three broad categories:

a) Temporary binder systems.

b) Binderless systems that seek to achieve flushability via combinations of fabric composition and mechanical bonding.

c) Combination of binder and mechanical approaches.

An alternative categorisation of the approaches that can be exploited to engineer wet wipe substrates based on underlying mechanisms that can lead to dispersibility is illustrated in Figure 2.2. Basel and Scholz (70, 71) describe the influence on dispersibility in terms of fibre-fibre interactions and the interaction between the fibre and turbulent water.

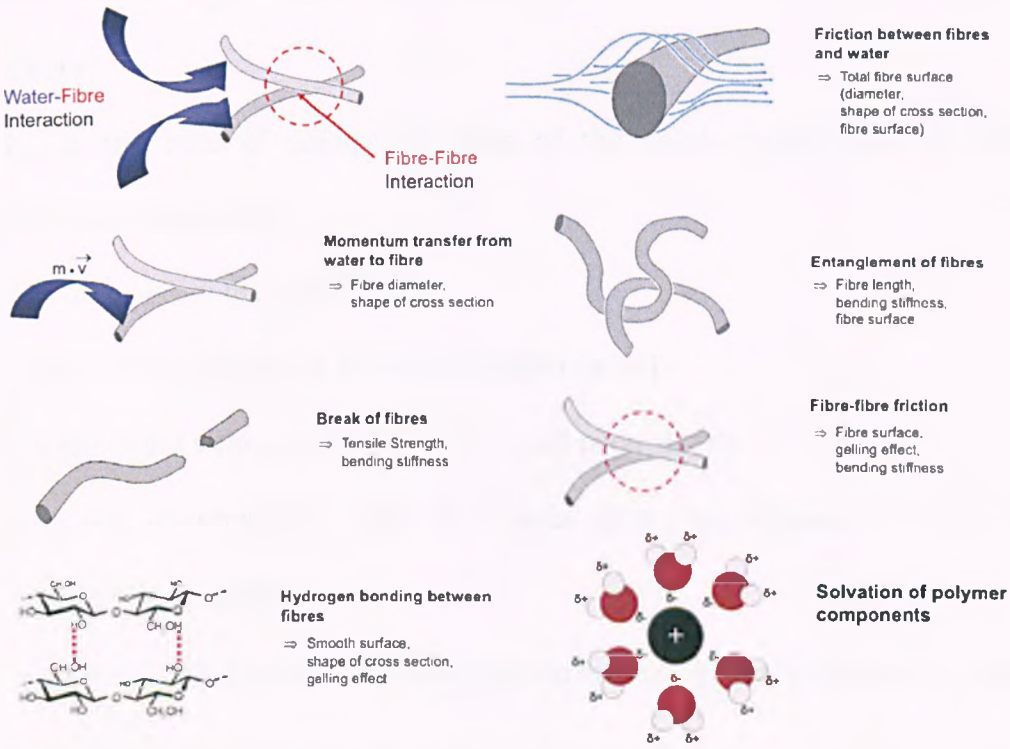


Figure 2.2 Mechanisms influencing the dispersibility of wet wipe substrates, adapted from Scholz (70)

They describe the fibre-fibre interactions as friction, entanglement, hydrogen bonding and fibre breakage. The fibre-water interactions are described as fibre-water friction in moving water and momentum transfer from water to fibres (collisions between water and fibres). The influence of composition, including solvable polymer is not considered; consumer products composed of 40% solvable components have been shown to disintegrate at a higher rate than those not containing any solvable materials (72).

Karadagli et al (72) showed that the disintegration rate (k_i) is related to the mechanical strength of the nonwoven substrate and the turbulence that it encounters after disposal. This relationship is given in equations 2.1 and 2.2.

$$R_{dis} = \frac{dM}{dt} = V\frac{dC}{dt} = K_i \times Re \times C \times V \qquad \textit{Equation 2.1}$$

Where:

R_{dis} is the rate of change in mass of the solid product due to physical disintegration ($g.s^{-1}$),

M is the mass of the product (g),

C is the concentration of the solid product ($g.L^{-1}$),

V is the liquid volume containing the solid product (L),

k_i is the disintegration rate coefficient (h^{-1}) that depends on the solid's mechanical properties, and

Re is Reynold's number representing turbulence in water (unitless), which is defined by:

$$Re = \frac{(\rho \times v \times d)}{\mu} \qquad \textit{Equation 2.2}$$

where:

ρ = density of water ($g.L^{-1}$)

v = average flow velocity ($cm.s^{-1}$)

d = depth of water (cm)

μ = viscosity of water ($g.cm^{-1}.s^{-1}$)

The equations suggest that the disintegration rate of the nonwoven could differ depending on where in the sewer network the wipe is situated. Initial turbulence during toilet flushing is likely to be high but for a very short duration. After this the volume of water is much reduced leading to very low levels of turbulence. Only in main sewer pipes, with larger diameters, will the combination of high flow velocity and high water depth be apparent for lengthy periods. The disintegration rate constant (k_i) has been found to increase with increasing turbulence which shortened the time for disintegration of flushable consumer products (73). The conditions that the wipe substrate are subjected to will affect how rapidly flushable products are likely to disperse. Within the sewer network these parameters will include pipe diameter, slope of the pipe, water depth, flow velocity and turbulence (74).

2.5 Approaches for improving the wet strength and dispersibility of fibre assemblies

Several researchers (75-77) have investigated factors contributing to the wet strength of nonwoven substrates, with particular focus on wet wipe applications. Most studies focus on long staple fibre (>30 mm) fabrics with limited research conducted on wet strength mechanisms in short staple fibre

(<15 mm) nonwovens. The methods employed to improve the wet tensile properties of nonwovens are reviewed. There is particular focus on nonwovens composed of short fibre (<15 mm) as these are commonly employed in commercially available flushable wipes (8, 78, 79). A review of the factors contributing to the wet strength of paper webs is included for completeness.

Typical mean wet tensile strength values of current nonwoven wet-wipe substrates are indicated in Table 2.1.

Table 2.1. Indicative wet tensile strength of current wipe substrates (80-82)

Fabric	Grade, Manufacturer	Manufacturing Platform	Wet Tensile Strength MD (N/50 mm)	Wet Tensile Strength CD (N/50 mm)
Dispersible	Hydraspun, Suominen	Wetlaid, Hydroentangled	8	5
Non-dispersible	Personal care wipe, Glatfleter	Airlaid, Chemical Bonding	11	4.5
Non-dispersible	Sawatex, Sandler	Carded, Hydroentanglement	80	24

Table 2.1 illustrates that in a typical wet wipe substrate that is designed to be dispersible, the wet tensile strength in both the MD and CD is low, i.e. less than 10 N/50mm. Essentially, the wet tensile strength is quite typically, uniformly low in all planar directions. Note also that in the dispersible wipe example shown in Table 2.1, the web formation manufacturing platform is wetlaid, which predominantly produces substrates from short cut fibres (≤15 mm) and wood pulp (1.5 - 3 mm). Use of a wetlaid platforms is unsurprising given that the technology is derived from the papermaking process used to manufacture

toilet tissue. Toilet tissue is composed mainly of short wood pulp fibres and therefore has poor wet strength, but rapidly disintegrates in the toilet and wastewater system. Factors affecting the wet strength of paper can also therefore be expected to be relevant to the engineering of wet wipe nonwoven substrates.

2.6 Compositional influences on wet strength and dispersibility

As is implied by Figure 2.2, the chemistry, dimensions, frictional and mechanical properties of fibres can all be expected to influence the strength of wet wipe substrates as well as their propensity to disintegrate during disposal. This section considers relevant previous work related to the development of wet tensile strength and the effect of composition on dispersibility. Cellulose, in the form of wood pulp and regenerated cellulose fibres, is the dominant material used in commercial flushable products (79). It is compatible with wastewater processing, therefore cellulosic materials are emphasised during this review.

The main approaches for imparting flushability to fibrous materials are listed in Table 2.2. The approaches consist of compositional changes, mechanical and chemical bonding. Some of the approaches combine mechanisms to optimise flushability performance.

Table 2.2. Flushable mechanisms of fibrous materials

Approach	Mechanism
Composition	Soluble fibre/binder Fibre dimensions Fibre cross-section Biodegradability
Mechanical bonding	Hydroentanglement Embossing Creping
Chemical Bonding	pH sensitivity temperature sensitivity reducing surface energy modification of friction binders with strength sensitive to changes in the ionic content of the wetting medium

The mechanisms given in Table 2.2 are discussed in sections 2.6.1 to 2.7.3.

2.6.1 Soluble fibres or binders

The ability of a wipe to disintegrate in an aqueous environment after disposal is critical to confer flushability. Including solvable materials in the composition of a wipe can help to increase the rate of disintegration under turbulent conditions (72). By incorporating a proportion of water-soluble material within the substrate it is possible to trigger disintegration in aqueous environments whilst maintaining strength in wet environments for a limited time period. This approach has been used in many dry-to-aqueous applications (predominantly sanitary products). Water-soluble polymers have been employed in flushable products in various forms. These include support of a fibrous network with water-soluble film/coating (83), intimate blending of non-water-soluble and water-soluble fibres (84) or the inclusion of water-soluble binders with non-soluble materials (85, 86).

A list of polymers included in these approaches is given in Table 2.3. These polymers have been incorporated in fibre and/or binder form.

Table 2.3 Soluble polymers used in flushable products (33-35, 37-39, 42, 46, 48, 49, 55, 83-111)

Polymer type	Polymer
Water-soluble vinyl polymers	Polyvinyl alcohol (PVA) Polyvinyl pyrrolidone
Polymers of acrylic acid	Polyacrylic acid Polymethacrylic acid
Modified starches	Dextrins Hydroxyethyl starch ethers Amine starches Phosphate starches Starch acetates
Cellulose derivatives	Carboxymethylcellulose Hydroxymethyl cellulose Hydroxyethyl cellulose Hydroxypropyl cellulose Hydroxyethyl hydroxypropyl cellulose Methyl cellulose Ethyl cellulose Epoxy derivatives of cellulose
Natural gums and alginates	Gum arabic Sodium alginate
Other polymers	Polyacrylamide Polyethylene oxide Polyethyleneimine Poly-acrylonitrile Saponified copolymers of ethylene and Vinyl acetate

All the polymers in Table 2.3 have limited use in wet wipes because they immediately start to solubilise when in contact with water. To be applicable in wet wipe products the polymer should not solubilise in the wetting liquid but be triggered when disposed of in the toilet, where there is enough liquid to fully saturate the wipes. In relation to the polymers indicated in Table 2.3,

approaches for manufacturing wet wipes using water-soluble polymers will now be discussed.

Jackson et al. (112) describe a nonwoven constructed from bicomponent fibres with a thermoplastic core and a sheath of water-soluble polymer (e.g. PVA or sulphonated polyester). The formation of a nonwoven composite of wood pulp and meltblown polymer is described by Pomplun et al (113, 114); through the use of a water-soluble polymer for the meltblown portion of the fabric, a water-dispersible fabric is achieved. Solvation of the water-soluble components for both these inventions can be delayed by careful selection of the sheath polymer combined with many of the mechanisms described later in this review.

Drach and Roberts (115) sandwiched a thermoplastic water-sensitive reinforcement grid between two fibrous webs. Through thermally bonding 3-25% of the reinforcement to the webs a water dispersible fabric is achieved. By keeping the wet pick-up of the wipe below 250% the product is reported to remain stable for up to 2 years, although this level of wet pick-up is lower than standard wet wipes (300-400%).

Konishi and Okada (116) describe a fabric constructed from a combination of short fibres (wood pulp), longer staple fibres (20 mm) of a non-soluble polymer (e.g. polyester) and water-soluble fibres such as carboxymethyl cellulose (CMC). The water-soluble fibre is prevented from immediate solvation by compressing the fabric structure to hinder water ingress and hence solvation.

Another method to impart flushability upon a wet-wipe is to bond the fibres using a water-soluble binder such as PVA in conjunction with a non-aqueous lotion. The water-soluble materials do not enter an aqueous environment until disposal and as a consequence have high strength during use and partially dissolve on entering the sewer network. However, the applications for this type of lotion system are very limited (45).

Whilst soluble fibres can be a valuable component in flushable products, their use in wet wipes is limited unless solvation can be prevented until disposal. As yet there are few methods of achieving this economically that work universally in all disposal environments.

2.6.2 Fibre tenacity

It is reasonable to expect the wet strength of the substrate to be influenced by the constituent fibre wet strength. Whilst cellulose is the preferred material for wastewater process compatibility, wood pulp and regenerated cellulose fibres, such as viscose, exhibit reduced tensile strength in wet conditions (117). Table 2.4 shows some expected wet and dry tensile properties of common regenerated cellulose fibres.

Table 2.4 Wet and dry tensile properties of some cellulosic fibres, adapted from Woodings (117).

Property	Viscose	Modal	Polynosic	Cupro	Lyocell
Water imbibition (%)	90–100	75–80	55–70	100	65–70
Dry Tenacity ($mN.tex^{-1}$)	200–240	340–360	350–400	150–200	400–440
Wet Tenacity ($mN.tex^{-1}$)	100–150	190–210	270–300	90–120	340–380
Dry Breaking extension (%)	20–25	13–15	10–15	7–23	14–16
Wet Breaking extension (%)	25–30	13–15	10–15	16–43	16–18
Wet Initial modulus ($mN.tex^{-1}$)	400–500	1000–1200	2000–2500	300–500	2500–2700
Degree of polymerisation	250–350	300–600	500–600	450–550	550–600

The data in Table 2.4 highlights the difference in dry and wet tenacity of common cellulosic fibres. For all regenerated cellulose fibres the tenacity is lower in the wet state compared to the dry state. Viscose fibres are characterised as having low wet tenacity values (≤ 150 $mN.tex^{-1}$) and high wet breaking extension (≤ 30 $mN.tex^{-1}$), even under conditions of low stress (118).

Lyocell (or Tencel) fibre offers increased wet tenacity, compared to viscose, due to its highly orientated, long crystallites, which exhibit low clustering in combination with a high amorphous orientation (119). The fibre has a tendency to fibrillate due to low lateral hold between the fibrillar structure (119). Lyocell has a degree of crystallinity of approximately 60%, compared to 40% for high-tenacity viscose rayon, measured by wide-angle X-ray diffraction (117). Substitution of viscose by lyocell has been found to improve both the wet and dry tensile properties of nonwoven fabrics (118, 120).

Table 2.4 also provides tensile data for other regenerated cellulose fibres, Modal, Cupro and Polynosic. Modal exhibits increased wet tenacity compared to viscose but decreased compared to lyocell. Lyocell is available commercially for nonwoven applications whereas Modal is targeted at home textiles and apparel applications (121). The cost structure of Polynosic and Cupro is relatively high due to high processing costs and not suited for use in large consumer markets, such as wipes.

Bertram's (75) research with hydroentangled cellulosic fibres found that Tencel (lyocell) produced the highest wet strengths compared to cotton and viscose. Bartholomew and Abercrombie (122) found that the fibre tenacity in cellulosic hydroentangled fabrics influenced wet strength to a greater extent compared to levels of entanglement. They attributed this behaviour to fibre swelling.

2.6.3 Fibre blend proportions

Another possible way of balancing the dual requirements of high wet tensile strength in the substrate and dispersibility is to manipulate the relative composition of the fabric by adjusting blend proportions thereby maximising tensile strength whilst maintaining dispersibility.

Takeuchi and Konishi (68) described the effect of blending 3-5 mm and 6-10 mm viscose fibres and a refined soft wood pulp with a fibre length between 3-4.5 mm. Bonding was achieved using hydroentanglement. The relationship between the obtained results for wet tensile strength and dispersibility are

shown in Figure 2.3. The dispersibility was measured according to a Japanese dispersibility test JIS P-4501, which is designed to test the disintegration performance of toilet paper. The test differs considerably to the developed WSP methods and is conducted in a standard 300 ml beaker with a magnetic disc rotating at 600 $r.min^{-1}$. The time until disintegration is measured and recorded. The pass criteria for toilet paper is >100 s (123). The dispersibility performance required to pass this test is much higher than for WSP methods.

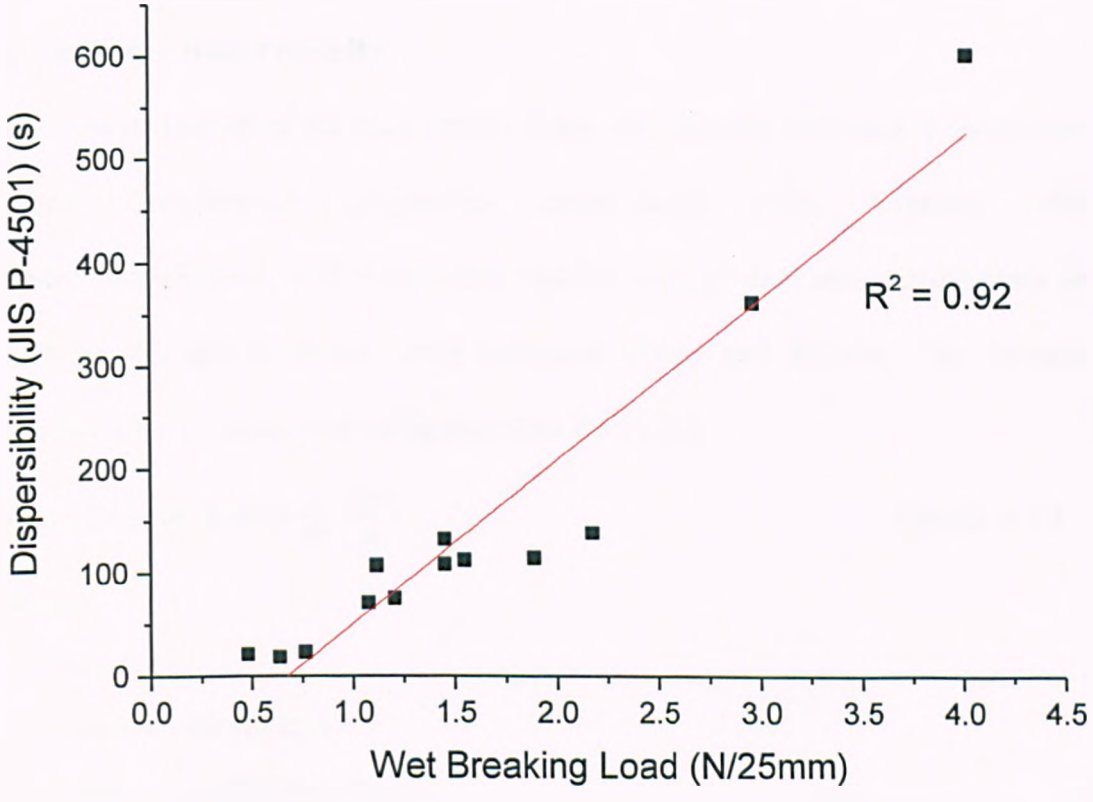


Figure 2.3. Relationship between wet strength and dispersibility of Takeuchi and Konishi fabrics (68)

The results in Figure 2.3 show an approximate linear relationship (R^2 = 0.92) between dispersibility and wet breaking load. As the wet tensile strength increases, the time for disintegration increases. The wet tensile strength was very low, below 3 N/25 mm; a strength that is unlikely to be commercially acceptable outside of Japan.

Experimentally, Woodings (76) observed reducing the diameter of viscose fibres resulted in stronger hydroentangled fabrics. He ascribed the effect to increased entanglement efficiency due to reduced fibre stiffness and increased number of fibres per unit volume. He also hydroentangled wetlaid fabrics composed of 8 mm, 0.77 dtex viscose, producing fabrics with similar dry tensile properties to 1.67 dtex, 38 mm carded-hydroentangled fabrics (76). The specific wet tensile strength of 1.7 dtex, 37 mm and 0.95 dtex, 8mm viscose fabrics was observed to be similar, between 50-60 $N.g^{-1}$ (75). In wetlaid-hydroentangled fabrics, low fibre linear density (0.95 dtex) has been observed to impart higher wet tensile strength compared with fibre of higher linear density (2.8 dtex) (75).

The evidence presented suggests that decreasing fibre linear density (and therefore diameter) leads to increases in the wet tensile strength of hydroentangled fabrics. Surprisingly, there is little evidence of how fibre diameter influences dispersibility. Scholz's (70) study suggests that reducing the fibre linear density from 1.7 to 0.9 dtex results in a decrease in dispersibility although fabrics with similar tensile strength showed similar dispersibility. Careful selection of fibre linear density will be required when engineering flushable wet wipe substrates.

2.6.5 Fibre cross-sectional shape

The influence of a fibre's shape factor on flexural rigidity has already been shown in equation 2.3, noting the affect of flexural rigidity on the strength of mechanically bonded nonwovens. The fibre cross-sectional shape may also be

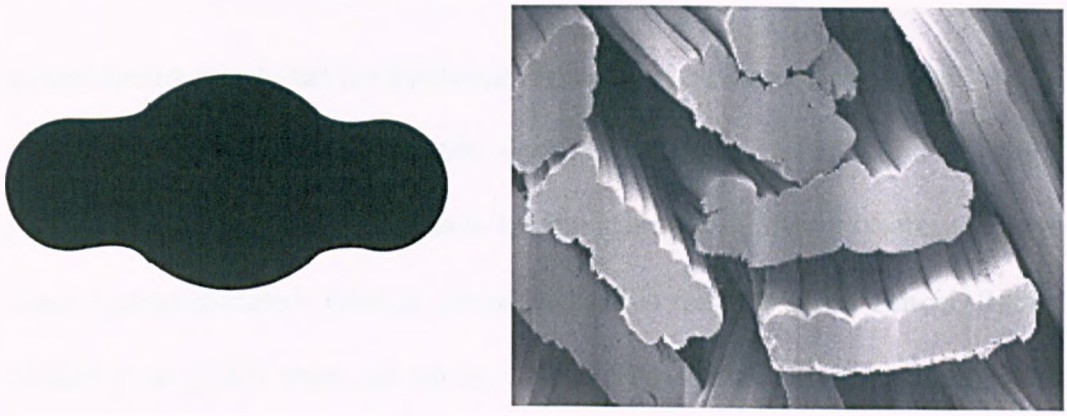
expected to influence the contact area between fibres in a fabric structure and affect both its tensile properties and a fabric's ability to disentangle.

Round cross-section viscose fibre has been observed to produce higher wet strength than flat and trilobal variants with the same fibre tenacities (75). This was attributed to the higher flexural and torsional rigidity of the flat and trilobal fibres reducing entanglement efficiency during hydroentangling.

Sulzmaier (126, 127) also observed a reduction in tensile properties when directly comparing flat and round cross-section viscose fibres. He reported that the MD and CD tensile strength was approximately one third lower for fabrics composed of flat cross section viscose than comparable fabrics made out of viscose with round cross section. Scholz (70) observed the same relationship of tensile properties with round and flat fibres, particularly when the sum of the applied pressure was over 100 bar.

Modification of fibre cross section has also been considered as a means to impart dispersibility. By careful selection of the fibre cross section, the disentanglement and dispersion of fibres could be enhanced by reducing the area of contact between fibres or by preventing full entanglement during bonding. Fibre-water interactions will also be influenced by the cross-sectional shape.

The cross section of a fibre produced by Clark and Shiffler (128, 129) is shown in Figure 2.4(a). They proposed a synthetic fibre cross-section of scalloped-oval cross-section to promote dispersibility in water.



(a) Fibre cross section - Clark and Shiffler

(b) Viloft dispersible viscose with flat cross-section

Figure 2.4 Fibre cross sections designed to enhance water dispersibility

A regenerated cellulose (viscose) product with a flat cross section has been marketed for flushable applications under the brand name Viloft (Kelheim Fibres GmbH) (126, 127, 130). The cross section is shown in Figure 2.4(b). Sulzmaier (126) reported faster dispersion (6 turns) of carded-hydroentangled fabrics with flat cross section compared to round cross-section viscose (41 turns) assessed using the tipping tube method. It is not clear from the work of Sulzmaier whether the improved dispersibility is simply a function of decreased tensile properties.

2.6.6 Fibre length

Fibre length is believed by many workers (68, 70, 94, 131-133) to be important because of its effect on tensile strength and dispersibility performance. Current

commercially-available flushable products are composed of short fibres ≤10 mm in length (79), including wood pulp, regenerated cellulose and cotton. Fibre lengths above 20-30 mm are normally associated with poor dispersion (55).

It is well documented that for hydroentangled fabrics, increasing fibre length is associated with increases in tensile strength (122, 134, 135). For example, Bertram (75) observed an increase in tensile strength of approximately 50% in wetlaid-hydroentangled fabrics composed of 4 and 8 mm Tencel fibres. Möschler et al (134) reported up to 50% increases in tensile strength when increasing the fibre length from 38 – 50 mm in carded-hydroentangled fabrics. When fibre fineness remains constant the fabric tensile has been reported to increase up to a maximum length of between 50–60 mm (135).

White (77) found that the pulp type had an influence on the wet strength of wetlaid fabrics constructed from 50:50 blends of pulp and 12 mm, 1.7 dtex polyester. For nominal 50 $g.m^{-2}$ fabric White recorded wet tensile strengths between 21.0 – 37.0 N/50 mm. The results suggest that pulp length contributed to wet strength as the highest strengths were attained using cotton linters (31 N/50 mm) and manila hemp (abaca) pulp (37 N/50 mm), which exhibited the longest fibre lengths.

Fundamentally, fibre length will be important in the dispersion mechanism because separated fibres, above a critical length are susceptible to "roping" as they twist together (55). To impart adequate dispersibility the fibre length

must be carefully selected. The aspect ratio of a fibre (length divided by the diameter) component is considered to be important in preventing roping (68), which leads to fabrics composed of fibres ≤10 mm being commonly employed in current flushable wet wipe applications (136). United States Patent 6,287,419 describes a hydroentangled fabric composed of a combination of short softwood wood pulp with regenerated cellulose fibres of different lengths. Up to 50% of the fabric is composed of a combination of 3-5 mm and 6-10 mm regenerated cellulose fibres (68). Wang (132) suggests that fibres should be shorter than about 12 mm to prevent roping, preferably about 6-8 mm. Scholz (70) found that nonwovens with a staple fibre length of 40 mm formed ropes. Although the material initially disintegrated into several pieces roping of the fibres was observed and prevented complete disintegration into single fibres.

The work of Jackson et al (114) suggests that fibres should be <15 mm in length but that roping is minimised using fibres <6.35 mm (about 0.25 inches). Further work by Jackson et al (133) reported that having 15% of the fibres with a length of 8 mm did not significantly impair the dispersibility of the product and prevented roping.

At the entry to wastewater treatment plants, the effluent is screened to remove bulk solids. The finest screens have a mesh size of approximately 6 mm. Any dispersed fibres must be capable of passing through the screens to be considered flushable. The ability of a fibre slurry to pass through an aperture has been observed to be influenced by fibre length relative to the screen as well as its inherent stiffness (137-139).

2.6.7 Fibrillation

Fibrillation is defined as the process of splitting into fibrils or thin filaments (140). The separation of fibres into their component fibrils serves to decrease fibre diameter and increase surface area available for bonding. This behaviour is common in cellulosic fibres, which exhibit microfibrillar structures (141). The refining process during paper making serves to fibrillate wood pulp fibres resulting in increased dry tensile properties in the final product (142). Tencel (lyocell) has received particular attention due to its high propensity to fibrillate (143), particularly in paper, wetlaid and hydroentangled nonwoven applications (117). Woodings (76) found that hydroentanglement pressures above 100 bar led to a tendency of Tencel to fibrillate, resulting in reduced air permeability, increased tensile properties and higher stiffness.

It is reasonable to expect that the effect of fibrillation on wet tensile strength and dispersibility would be similar to those observed with changes in fibre linear density (and therefore diameter), detailed in 2.6.4. A number of researchers (136, 144-146) have sought to take advantage of a fibre's fibrillation behaviour to maximise tensile properties whilst maintaining dispersibility.

Collins, Slater and Rahbaran (144) utilised the fibrillating propensity of Tencel fibres to improve wet strengths of wetlaid pulp-Tencel (80:20) blends bonded by hydroentanglement. Refining the fibres prior to laydown increased the wet tensile properties by over 50% (1.9 - 3.3 N/50mm). These values, however, are still inherently low and commercially unsuitable for wet wipe applications. The

wipes exhibited high levels of dispersibility using the tipping tube method, with over 100% of the wipe passing through a 3 mm screen.

Takeuchi (145) employed a similar approach using fibrillated polynosic viscose. The fibres were pre-fibrillated prior to wetlaying and then subsequently hydroentangled. The wet tensile strengths achieved were higher (>6 N/50mm) than reported by Collins et al but the composition utilised increased proportion (≥50%) of viscose (both fibrillated and non-fibrillated) to increase levels of mechanical bonding. The dispersibility was measured according to JIS P-4501, as detailed in 2.6.3, with the wipe dispersing within 100 seconds. A further extension of this approach is described by Tanio et al (136), employing a blend of fibrillated rayon fibres of different lengths (between 3-5 mm). Wet strengths above 10 N/50 mm were obtained but the fabrics were composed of 80% fibrillated 1.7 dtex, 5mm viscose fibre and only 20% wood pulp. The fabrics took over 300 s to disintegrate measuring using the JIS P-4501 method.

Takai and Konishi (146) also employed wetlaying and hydroentanglement with a fibre blend of wood pulp and microfibrillated cellulose. The microfibrillated cellulose (CELLISH KY 100G), with a mean fibre diameter of 0.001 – 0.1 μm, provides enhanced hydrogen bonding of the structure, preventing immediate dispersion. Compositions containing 50% woodpulp, 30% 1.1. dtex, 5 mm viscose and 20% microfibrillated cellulose delivered a wet tensile strength of <5 N/50 mm and dispersiblility <100 s measured using JIS-P4501.

Fibrillated fibres can offer some useful properties when designing a flushable wet wipe substrate. Some of the compositions described offer good dispersion performance and moderate (≤11 N/50 mm) wet tensile strength. The main disadvantage of fibrillated fibres is their high cost compared to standard non-fibrillated textile fibres, which goes some way to explain their lack of penetration into commercial applications. The proportions required to impart high wet tensile properties is also very high. The resultant compositions are likely to be very expensive and not commercially viable.

2.7 Influence of bonding

The bonding method and degree of bonding could reasonably be expected to influence tensile strength and dispersibility of a flushable wipe substrate. Chemical and mechanical bonding are the main methods employed in commercial flushable wipes as they have the potential to be reversed to enable dispersion (147). The application of thermal bonding has been limited by the non-biodegradable nature of the bonding systems available (8). Hydroentanglement is the dominant method for mechanical bonding, mirroring the technology used in non-flushable wipe applications, which is dominated by drylaid-hydroentangled substrates (148).

2.7.1 Mechanical bonding; hydroentanglement

Mechanical bonding is attractive for flushable wipe substrates because the fibres are entangled together and held by friction. In a wet state the friction forces are reduced and it is then possible to disentangle the fibres with turbulence and mechanical forces upon the wipe. The final properties of the

nonwoven are influenced by both the fibre and process parameters. Möschler (134) listed the main fibre and process parameters that can influence the strength in hydroentangled nonwovens in Table 2.5.

Table 2.5. Fibre and Process variables that influence the strength of hydroentangled nonwovens, adapted from Möschler and Albrect et al (134, 149)

Fibre Influences	Process Influences
Polymer • density • stress-strain characteristics • structure e.g. fibrillation propensity • stiffness • frictional characteristics • fibre modification	**Web structure** • areal density • fibre orientation **Speed**
Geometry • length • fineness • crimp • cross-sectional shape • surface structure	**Support screen structure** • weave type • opening shape and size • wire gauge
Others • finish • wettability	**Water-jet** • cross-sectional shape • diameter • number of jets • arrangement/distribution • Applied energy/pressure • angle

The important fibre properties and their influence on tensile strength and dispersibility have been discussed in 2.6. The process variables will also influence the final properties of a hydroentangled material. The resultant fabric properties after hydroentanglement are influenced by the energy introduced to the web. The specific energy consumed by a unit mass of fibres is dependent on the water pressure, flow rate and residence time of fibres under the jets (belt speed).

The specific energy inputted during hydroentanglement has been observed to have a direct correlation with fabric strength. Mao and Russell (125) found that carded-hydroentangled fabrics composed of viscose fibres increase rapidly in tensile strength above a certain energy threshold until high impact energy starts to result in structural degradation of the constituent fibres decreasing tensile strength. Zheng et al (150) reported a similar relationship of increasing tensile properties with specific energy, increasing to approximately 12 $MJ.kg^{-1}$; increasing applied energy between 12-45 $MJ.kg^{-1}$ resulted in no further increase or decrease in tensile properties. Connolly and Parent (151) reported the tensile strength development of carded and crosslapped 50:50 polyester-viscose fabrics with increasing specific energy. 90% of the tensile strength was achieved with applied specific energies below 1.0 $kw.hr.kg^{-1}$; fibre length and linear density were not reported.

Many of the process variables in Table 2.5 are taken into account by calculating the specific energy (e.g. speed, web areal density) inputted. The nature of the support screen is not accounted for and has been observed to be critical for developing the desired properties in hydroentangled fabrics. The size of the openings is considered important when processing short fibres such as wood pulp. Gahide (152) found that if the screen is too open then many of the shorter fibres were lost from the web so that it could not be removed from the screen. Andersen (153) recommended 38—58 mesh as the optimum hydroentangling conveyor. Mesh size relates to the size of openings in a woven conveyor and is defined as the number of openings per unit width ($n.2.54\ cm^{-1}$). At low mesh sizes the open area of the mesh is high, reducing as the mesh size increases.

Due to short fibre nonwovens showing increased dispersibility wetlaid, hydroentangled flushable wipes composed largely from wood pulp and regenerated cellulosic fibres have been developed (58, 59, 120, 154). The flushability mechanism relies on making the product as strong as possible with mechanical bonding without preventing dispersibility.

Manning et al (58) were the first to suggest such an approach, disclosing a binder free, hydroentangled web material consisting of up to 15-30% short-cut (12.5 mm) viscose fibres and wood pulp. Manning et al observed an inverse relationship between wet strength and dispersibility. As the wet tensile strength increased, the dispersibility decreased. Viazmensky and Benjamin (59) suggested an improvement to the work of Manning et al to improve wet tensile strength, wet thickness and wet toughness of the wipe. They added 1-2% of a wet strength additive (polyamide epichlorohydrin) to the cellulose fibres during wetlaying, claiming a cumulative effect of the additive and mechanical bonding on resultant fabric strength. 1 wt.% of the wet strength additive doubled the wet tensile strength but stopped the wipe from dispersing. Annis and McDade (155) offered the most recent improvement by substituting viscose for lyocell. Lyocell's high wet strength increased the wet tensile strength of the resultant fabrics by 50% compared to viscose, although the absolute value is still very low (<5.5 N/50mm). A small proportion (1-5%) of synthetic bicomponent binder fibre was also added to enhance fabric strength following thermal bonding. Some dispersibility was conferred to the substrate but the sample did not fully disperse when treated for 165 seconds in the

tipping tube test. This composition is commercially available as the Hydraspun product offered by Suominen (previously Ahsltrom).

2.7.2 Other mechanical bonding approaches

The approach with hydroentanglement is to confer enough bonding to maximise tensile strength whilst maintaining dispersibility. For other approaches, fully bonded fabrics are used and then post-treated to disturb the bonds and confer dispersibility. The techniques that have been employed include creping (156), embossing (157) or compression. Brennan (158) proposed nonwoven webs comprised of non-thermoplastic fibres with discrete compressed sites imparting lines of weakness. The fabric is designed to fail along the weakened areas when the web is subjected to mechanical forces such as those during disposal in the sewer network. Noda et al's (159) approach is similar and involves mechanically weakened the fabric in longitudinal lines by passing the fabric through intercalated rollers. This type of approach results in improved dispersibility but reduces wet tensile strength considerably. The fabrics are likely to disperse into large sections rather than individual fibres.

2.7.3 Chemical Bonding

Chemical bonding involves the application of a liquid-based bonding agent to a fibrous web. Through the application of a binder whose binding behaviour changes depending on the local environment, e.g. pH, ionic strength or temperature, it is possible to obtain both an adequate wet tensile strength and good dispersibility.

Chemical binders have been used extensively in flushable wet wipes. Mechanisms for 'triggering' binders to weaken due to an external stimulus have been designed. Many of the approaches incorporate water-soluble fibres or binder which are rendered insoluble by the composition of the lotion. When the wipe is discarded and the concentration of the lotion is reduced, solvation occurs and the wipe strength decreases, triggering dispersion. Much of the intellectual property centres on ionic interactions, which can be affected by divalent ions in hard water.

2.7.3.1 Ionic - Salting-out of water-soluble polymers

Salting-out is described as the decrease in solubility of a non-electrolyte in ionic solutions (160). By incorporating water-soluble components (e.g. fibre or binder) and preventing solvation by inclusion of an ionic complexing agent in the wet wipe lotion (e.g. an electrolyte) wet strength during use can be maintained. Once the wet-wipe has been used and disposed of in an aqueous environment, the concentration of the complexing agent is decreased as a result of dilution, meaning solvation can then occur. The salting-out coefficient (K_S) is described by Setschenow's equation (equation 2.4) (161, 162):

$$log(S°/S)/ C_s = K_S \qquad \textit{Equation 2.4}$$

where:

$S°$ is the solubility of the substance in pure water (mols/L)

S is the solubility in the salt solution (mols/L)

C_s is the equivalent concentration of the salt.

Although it is impossible to derive an absolute order, Randall and Failey (163) suggested negative ions in the order of their decreasing salting-out effect; hydroxide; sulphate and carbonate; chlorate, bromate, chloride, acetate, iodate and perhalide, bromide and iodide, nitrate. For positive ions: sodium, potassium, lithium, barium, rubidium, calcium, nickel, cobalt, magnesium, ferrous, zinc, cesium, manganous, aluminium, ferric and chromic, ammonium and hydrogen. Hey et al suggested an order of sodium salts for salting out polyethylene glycol: $OH^- < SO_4^{2-} < HPO_4^{2-} < CO_3^{2-} < PO_4^{3-}$. (164)

The main combinations of water-soluble polymer and electrolyte used in flushable applications are listed below:

- Modified guar gum and borate ions (53)
- PVA and lotion containing boric acid (40, 41, 43, 54, 56, 57, 131, 165-167), PVA binder and lotion containing low levels of boric acid and sodium bicarbonate (168), PVA and lotion containing sodium sulphate (169), PVA and lotion containing a water-soluble carboxylate such as sodium tartrate or potassium tartrate (170)
- Vinyl acetate latex binder stabilised with PVA and a small amount of poly(acrylic acid) (171)
- Hydroentangled PVA blend with solubility inhibitors such as water-soluble organic salts (e.g. sodium tartrate), water-soluble inorganic salts (e.g. sodium sulphate) and water-soluble boron compounds (e.g. Boric acid) (172, 173)
- Binder comprising of sulphate esters of cellulose which form aqueous gels in the presence of potassium ions (54)

- Carboxymethyl cellulose binder and calcium chloride (174), Carboxymethyl cellulose binder, having a degree of substitution of 0.30-0.60, and sodium carbonate (175), Carboxymethyl cellulose binder and a polyvalent metal ion (176)
- Methyl Cellulose and sodium sulphate with the addition of a small amount of colloidal silica (177)

Problems have been observed with salting-out polymers in hard water areas, where divalent cations of calcium and magnesium are present in high concentration (178). Multivalent cations are known to bind strongly to carboxylate groups, potentially leading to ionic crosslinks and insolubility (179). When the concentration of salt is diluted in hard water, the cations continue to salt-out the polymer, preventing solvation.

Kimberly Clark's ion-sensitive polymers are a development of the acrylic acid terpolymers developed by Lion Corporation (55, 180, 181), Ion-sensitive acrylic acid copolymers comprised of a combination of acrylic acid monomers and acrylic ester (alkyl acrylate) monomers capable of free radical polymerisation into a copolymer are employed (182-184). 2-acrylamido-2-methyl-l-propanesulphonic acid (AMPS) and its sodium salt (NaAMPS), containing the softer sulphonate anion, are included to be less interactive with multivalent ions present in hard water, particularly Ca^{2+} and Mg^{2+} ions. A further development of this concept involves the inclusion of a cationic polymer (2-[methacryloyloxy]ethyl) trimethyl ammonium chloride. The cationic nature of the polymer results in less sensitivity to divalent cations (up

to 200 ppm) that occur naturally in hard water. The inclusion of less than 10% sodium chloride in the wetting lotion protects the binder from solvation until aqueous dilution on disposal in the sewer network (60, 111, 178, 184-187). In order to achieve the desired product performance while maintaining product dispersibility after disposal, the salt responsive polymer molecular weight and composition must be tailored to achieve the best balance of wet-strength and dissolution rate (179).

Farwaha (188) describes a binder for a fibrous web, comprised of a salt-sensitive copolymer of vinyl acetate, crotonic acid and a vinyl ester. The binder is reported to achieve wet strength of at least about 14.5 N/50mm in a 10% NaCl solution but wet strength of less than 0.1 N/50mm in deionized water (189). The approach utilises an emulsion copolymer of ethylene and vinyl acetate (EVA) in combination with a water dispersible copolymer of carboxylic acid (acrylic acid), acrylate monomer units (hydroxypropyl methacrylate), and N-alkyl acrylamide units (N-tertiary octyl acrylamide), which is non-dispersible in aqueous solutions containing at >0.5% inorganic salt.

Other researchers have employed alternative binding chemistry with the same basic mechanism of working. These include an emulsion of polymethylmethacrylate (PMMA) and a water-soluble, salt-sensitive adjuvant such as copolymers of polyethylene glycol and polybutylene glycol (190). A water dispersible cationic polyurethane binder which contains condensation residues of a polyisocyanate with a biodegradable polycaprolactone (191). A temporary wet strength resin based on glyoxalated polyacrylamide polymer

(192, 193). A water dispersible, low molecular weight, branched co-polyester hot-melt adhesive containing a sulphomonomer (194, 195). A sodium cellulose acetate sulphate binder with a low degree of substitution (196) and a non-water soluble emulsion polymer, stabilised by acrylic or methacrylic acid (197).

2.7.3.2 Surface energy and coating with hydrophobic polymers

One approach to prevent dispersion of the wipe until disposal is to increase surface energy by inclusion of a protective hydrophobic barrier to prevent immediate contact with water molecules. This is achieved through coating water-soluble fibres or films with hydrophobic polymers. Hydrophobic coatings employed include polypropylene (198), polyvinylidene chloride (199), polyethylene (200), polyethylene mixed with wax, modified with ethyl vinyl acetate or synthetic rubber (201, 202), ethyl vinyl acetate polyethylene or cellulose derivatives such as ethyl cellulose or starch (202), polybutylene succinate polymers (203), colloidal polyethylene and delaminated clay (204) and water repellent oil, wax or resin (47). The application of this method of imparting dispersibility is limited in practice. Wet wipes require high levels of absorbency to be able to function correctly, which will be compromised by the hydrophobic coating. This approach is particularly suited to those applications which are dry during use such as packaging or release liners.

2.7.3.3 Dispersion triggered by changes in pH

The integrity of a pH-sensitive polymeric binder may be altered by increasing or decreasing the pH of the local environment; the binder may be rendered insoluble in one pH range but solubilise in a different range. pH-sensitive polymers have weak acidic (e.g., carboxylic acid) or basic (e.g., ammonia)

groups included in their structure that either accept or release protons in response to a change in the environmental pH (205). This behaviour has been applied in the design of flushable materials. By bonding the fibres in the wipe with a binder composition that has high strength in liquids with acidic pH but undergoes a reduction in strength in more neutral pH, dispersion can be triggered. The pH of wastewater generally shows little variation from the natural pH of water from the local environment, between pH 6-8 in the UK. Employing a binder which has high strength at pH 4 but decreases in strength from pH 4-7 allows the wipe to disintegrate when subjected to turbulence in the wastewater system.

Binder systems proposed for this approach include copolymers of acrylic acid-acrylic ester (206, 207) although these polymers required low pH (2-4), which is known to cause skin irritation in cosmetic applications. Binders from a copolymer of glyoxal and polyvinyl alcohol (44) functioned at higher (3-5) pH but included boric acid which is no longer permissible in cosmetic applications. A copolymer of a carboxylic acid (e.g. acrylic acid, methacrylic acid) and a styrene terpolymer, were reported to be insoluble below pH 6 and soluble at higher pH values (208).

Flushable nonwovens comprised of bicomponent fibre with an alkali hydrolytically degradable core, such as polylactic acid and water-soluble outer sheath (e.g. PVA) have been developed (209). The resultant fabrics can be dispersed in aqueous environments above pH 9.5 (e.g. commercial laundering)

and would not work in normal wastewater, therefore these approaches are unsuitable for flushable wipes (209, 210).

Overall, changes in the solubility or binder strength triggered by pH is flawed as a mechanism of dispersibility. The pH over which significant changes in properties occur tend to occur at the extreme ends of the pH scale, from either highly acidic or highly basic to neutral. These conditions are not suitable for skin contact therefore the application of pH triggerable systems is limited for commercial flushable applications; they could be suitable for bathroom cleaning wipes but this is only a small sub-section of the overall flushable wipes market (8).

2.7.3.4 Dispersion triggered by changes in temperature

Some hygiene applications have sought to exploit the difference between the ambient temperature of mains water and human body/body fluids to trigger the solvation of temperature sensitive polymers used to bond the product together. At temperatures above 30°C, the temperature sensitive binders retain high levels of wet strength, when disposed of in main water (<23°C) the binder loses integrity and solvation occurs enabling the fibre network to disintegrate when subjected to turbulent flow in the sewer network. Polymers that undergo a solution liquid-liquid phase transition in response to variation of the temperature are the most widely studied type of thermoresponsive polymers (211) and the type used in most in flushable applications (212-214). If phase separation occurs at an elevated temperature, this is referred to as lower critical solution temperature (LCST). Polymers that exhibit LCST close to 25°C

are employed as the binder in flushable applications. Polymers employed are commonly alkyl or hydroxyalkyl substituted celluloses and derivatives, such as hydroxypropyl cellulose (212-214), which is insoluble in water above 15°C.

The use of temperature sensitive binders is limited to hygiene applications as they require temperatures above 25°C (e.g. provided by the body) to remain insoluble and maintain product integrity. Wet wipes are commonly used in ambient temperatures, which would solubilise the binder and reduce product strength during the use phase.

2.7.3.5 Modification of fibre friction

It is reasonable to expect that reducing the wet sliding friction of fibres within a wipe would lead to an increase in dispersibility. Lynch (215) modified the frictional performance of hydroentangled regenerated cellulose fibres by phosphorylation, decreasing the wet coefficient of sliding friction (f_w) of the fibres from 0.3-1.3. This approach is likely to increase dispersibility but at the expense of wet strength, making it unsuitable for wet wipe applications. A similar approach employing partial carboxymethylation of regenerated cellulose fibre has also been investigated but resulted in fabrics with very low wet strength, less than 1 N/50 mm (216). Bildhauer (217) modified the friction of viscose-pulp fabrics through the incorporation of silicone fibre finishes. He noted that the dry strength was relatively unaffected but the wet strength decreased considerably.

2.7.3.6 Commercial flushable products using chemical bonding

Speciality papers and wetlaid nonwovens commonly include chemical binders in the fibre furnish to improve wet strength. 1-2% addition of Polyamideamine-epichlorohydrin (PAE) resin is widely used as a wet strength additive. Compared with other chemical binders such as urea formaldehyde and melamine-formaldehyde resins, PAE imparts wet strength over a wider pH range (218). Exemplars of wet wipes utilising PAE are disclosed by Rydell (156), Collins et al (144) and Viazmensky and Benjamin (59). The application of this binder type is limited in flushable applications because the dispersibility performance is compromised by its addition due to the binder not being triggerable.

Chemical spray-bonding was also employed when manufacturing dispersible airlaid webs. AIRspun, manufactured by Buckeye, uses a longer fibre web with a binder with limited water solubility (147). A lotion with only small amounts of water (100-300% by weight) is employed to prevent solubilising the binder (147). This product was removed from the market due to issues with dispersibility.

2.7.3.7 Combination of two or more bonding methods

A common strategy for improving the wet strength of fibrous structures is to combine multiple bonding methods to enhance product strength. For example, wetlaying in combination with hydroentanglement and thermal bonding (bicomponent thermoplastic), was employed by Annis and McDade (120). Mechanical bonding (hydroentanglement) followed by chemical bonding are

also often employed, as described by Viazmensky and Benjamin (59). These approaches improve wet strength but at the expense of dispersibility.

2.8 Review of the wet strength of paper

Toilet papers are accepted by the water industry as compatible with wastewater systems. They are released into wastewater systems in large quantities, it has been observed that 19.4 g/capita/day is disposed of in the sewer network in the UK (219). Compared to wet wipes they are considered highly dispersible (18) and are manufactured on a wetlaid platform therefore, previous studies of the wet strength of paper are instructive for identifying potential approaches for improving the wet tensile strength of nonwoven substrates containing short fibres.

Toilet papers are manufactured predominantly from cellulosic fibres (wood pulp) with addition of various chemicals e.g. binders, fillers, adhesives, color pigments, and scents (74). Building on the investigations of Lyne and Gallay (220, 221) into the strength of wet webs of wood pulp, there is broad agreement in the conclusions of all the researchers at low solids content (~25% and below), i.e. high levels of liquid saturation. The probability of fibre breakage is very low as applied stresses are considerably lower than the breaking stress of the fibres. It is suggested that the substrate's wet strength results from multiple factors including frictional resistance to fibre separation and disentangling, surface tension in the liquid medium and inter fibre bonding (222, 223).

In the dry state, the tensile strength of wood pulp webs is largely determined by a combination of the fibre strength and the bond strength at the fibre intersections. During tensile failure both fibres and bonds break, the extent of which is determined by the relative strengths. Webs of wood pulp exhibit much lower tensile strength in wet state and fibre breakage is not apparent following tensile break (224). Liquid bridges at fibre cross over points are suggested to exert an attractive capillary force on the fibres which holds them together, arising from the meniscus in the liquid bridge exerting Laplace pressure. Tejado and van der Ven (224) reported that the sum of the theoretical capillary forces, which need to be overcome in order to break the wet web, were an order of magnitude lower than those observed in practice in wet paper. They concluded that the capillary forces are too low at low solids content (i.e. high water content) and suggested that friction as a result of fibre entanglement is the dominant mechanism. The relationship is shown in Figure 2.5, where *a* is due to entanglement friction, *b* is due to hydrogen bonding and *c* is a cumulative strength of both phenomenon.

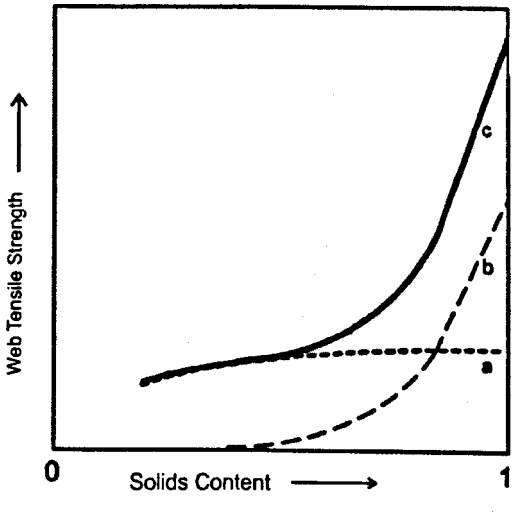


Figure 2.5 Wet web tensile strength of paper as a function of solids content, adapted from Tejado (224)

Figure 2.5 shows that in the dry state (solid content = 1) the mechanism of tensile strength is derived from a combination of entanglement friction and hydrogen bonding, with hydrogen bonding being the dominant force. As the solid content reduces (i.e. water content increases) towards 0, the dominant force becomes entanglement friction. At solid content <0.4 the contribution of hydrogen bonding to tensile strength is very low.

Oliveira (225) reported the addition of cellulose microfibrils enhanced wet web strength, indicating strongly that fibre entanglement is the major interaction responsible for keeping the swollen fibres together at low solids content; especially in the region where neither capillary forces nor hydrogen bonding dominate.

This information is useful when designing flushable wipes that are mechanically bonded. It suggests that entanglement friction is going to be the dominant force holding the fibres together. This is an important influence on wet tensile properties but also dispersibility in the sewer environment.

2.9 Summary

There are currently only two commercially-available dispersible wet wipe substrates, Hydraspun from Suominen and products based on Kimberly Clark's ion-sensitive technology. These two competing technologies represent the current state of the art in flushable wipe technology. Both utilise short fibre (<15 mm) technology platforms, Hydraspun is wetlaid and Kimberly Clark (KC) airlay their material. Neither material can be considered ideal as a flushable

wipe, the KC wipe has high wet tensile properties but disperses slowly whilst Hydraspun offers more rapid dispersibility but at the expense of low wet tensile properties (147). The KC binder technology is relatively expensive and heavily patent protected to prevent competition (147). Buckeye's Airspun product was withdrawn from the market after a relatively short period. Therefore there is a real need for new flushable technologies with high wet strength during use and rapid dispersibility after disposal that are compatible with wastewater treatment processes.

Reviewing the current test protocols has identified a common set of performance requirements to confer flushability to a wipe. The performance required includes conveyance through the disposal network (including pipes and pumps), settling, dispersibility and biodegradability. Wastewater treatment works (WwTWs) are designed to primarily process human excreta and toilet paper. Toilet paper is predominantly constructed from cellulosic wood pulp fibres 1-3 mm in length and rapidly disperses in water. To confer compatibility of the nonwoven wipe with current WwTW processes, the fibre selection should ideally be limited to cellulose. Alternative biodegradable materials have been considered as raw materials for flushable products, these include blends of thermoplastic starch and polyesteramide (226), polyhydroxyalkanoate, polyalkylene succinates or polycaprolactone (227, 228) and polylactic acid (229). These polymers are biodegradable but their commercial application in wet wipes has been limited by their relatively high cost.

Cellulose is the dominant material in flushable wipes, accounting for over 75% by weight (8). It's proven compatibility with wastewater treatment processes, biodegradability and relatively low cost make the material commercially attractive. Wood pulp and regenerated cellulose fibres, such as viscose and lyocell, predominate in flushable wipes. Mixtures of pulp and longer fibre are commercially acceptable but fabrics comprised of 100% pulp exhibit very low wet strength (230), <2 N/50 mm. Substitution of viscose content with higher tenacity cellulosic fibres, such as lyocell, has been observed to increase the wet and dry tensile properties of pulp-based fabrics by over 40% (120).

Dispersibility is key to the product's performance, as the filtering screen aperture size of the fine screens at the inlet of wastewater treatment works or outlet of Combined Sewer Overflows (CSOs) in the UK is generally less than 6 mm, which means any gross solids larger than this will be filtered out and disposed of (14, 231). Technology platforms associated with fibres greater than 20 mm in length such as carding have limited applications in flushable wipes. Carded-hydroentangled wipes are associated with the strongest wet tensile strengths but they have been found to disperse poorly (126, 127). Scholtz observed incomplete dispersion of 40 mm long fibres due to the fibres roping (70). Short fibre (<20mm) web forming technologies of airlaid and wetlaid are preferred to assist dispersibility.

The composition of a flushable wipe is critical to its function. Changing the fibre length, linear density and blend proportion have all been observed to affect wet tensile strength and dispersibility, although the effect of variation is not well

understood. Keeping all other parameters the same, decreasing the linear density whilst increasing the fibre length and proportion of longer fibre in the wipe can all be expected to increase wet tensile strength at the expense of dispersibility. Dispersibility is considered by some to be inversely proportional to wet tensile strength (147) but the evidence for this is not clearly presented in the literature and is worthy of further research. Pre-fibrillating fibres to reduce their diameter is observed to result in small increases in wet strength but decreases dispersibility markedly. The high cost of these prefibrillated fibres makes them unlikely to be useful in Fast Moving Consumer Goods (FMCG) markets such as wet wipes.

Mechanical bonding via hydroentanglement offers opportunities for engineering flushable wet wipe performance. After hydroentanglement, the fibres are held together by friction, which can be reduced in a wet state. The ability to disentangle the fibres with turbulence and mechanical forces upon the wipe has been observed but the mechanisms behind this are not well known. Further research is required to understand how disentanglement can occur and confer dispersibility. The final properties of the nonwoven are influenced by the hydroentanglement process parameters, in particularly specific energy and conveyor design. The literature is mainly focused on materials comprised of longer fibres (>20 mm) so further investigation is required to understand the process-structure-property relationships of short (<15 mm) fibre materials. The review of the wet strength of paper suggests that entanglement friction is the dominant force that will hold a wipe together in the wet state.

Modification of fibre cross-section has been observed to influence the mechanical bonding of hydroentangled wipe structure resulting in fabrics with reduced wet strength and increased dispersibility. Regenerated fibres with a non-round cross-section are available commercially but tend to have increased linear densities (>3 dtex), due to the complexity of spinning, and cost. The increased linear density can negatively affect the final properties of the wipe compared to finer, round cross-section fibres.

Binders with an environmental response are often employed for imparting increased wet strength properties, which reduce on contact with large volumes of water. Most of these approaches only work in idealised conditions, e.g. in very soft or deionised water where cationic interaction is limited. Natural fluctuations in local environments can hinder binder solvation and subsequent dispersion. There is also a large patent estate in this field, which prevents commercial exploitation. In addition, many of these binding chemistries are not compatible with WwTW processes, the ideal solution would include cellulose-based binder systems. Carboxymethyl cellulose (CMC) is of interest for further investigation as a binder as it is relatively cheap and readily available on a commercial basis. The ability of CMC to be salted out in solution offers the potential to improve wipe tensile strength through the addition of electrolytes to the wetting lotion, which can be diluted on disposal in an aqueous environment, reducing the tensile strength. Limited academic studies have been conducted with CMC bonded wipes and is worthy of further research on this basis. The approach is particularly interesting in combination with mechanical bonding. Bonding intensity could be reduced offering the potential

for increased dispersibility whilst a CMC binder offers the potential for maximising wet strength during use. Very little work has been conducted in this area.

Based on the literature, further research is required to elucidate the extent to which aspects of fibre composition, mechanical bonding, friction, fibrillation and chemical bonding can be engineered to enable a satisfactory balance of wet tensile strength and dispersibility. With regard to wet tensile strength, no existing commercially utilised product concurrently meets the requirements of a threshold wet tensile strength of 15 N/50 mm and ≥95% dispersibility (12.5mm apertured screen) performance, in accordance with the current flushability guidelines. 12.5 mm screen has been selected on the basis of compliance with the current third edition of the WSP Flushability guidelines (29) for dispersibility (GD3). An idealised dispersibility target would be 100% passage through a 6.3 mm screen as these are the dimensions commonly found at the inlet to wastewater treatment plants (18). This forms the basis of an aspirational specification for this research.

Chapter 3

Experimental Materials and Methods

This chapter details the equipment, materials and methods employed during the course of this research. It is included here as one chapter because many experimental methods were repeatedly used as means to determine aspects of fabric structure and properties.

All the raw materials used in the manufacture of experimental samples for testing were selected on the basis of their compatibilities with nonwoven manufacturing processes and sewer disposal. As explained in section 2.9, the market leading water dispersible wipe technologies rely upon web substrates comprising a blend of wood pulp and fibres of small mean fibre length (~4-8 mm) bonded by either hydroentanglement or a binder whose adhesive strength is dependent on the surrounding liquid medium. Accordingly, based on these insights, the present research studied substrates made using short-fibre web formation techniques (wetlaid and airlaid) and bonded by hydroentangling.

3.1 Raw materials

Fibre specifications and a list of the chemicals employed in the study are summarised in Table 3.1. All the raw materials, including the wood pulps were selected for their compatibility with airlaid and wetlaid manufacturing

processes. Irving Softwood Craft Pulp, is a northern bleached softwood kraft which is oxygen delignified, and chlorine-free (232). Industrially, it is commonly used in wetlaid nonwoven manufacture for products such as wet wipes and tea bag papers and was used to form all the wetlaid experimental wipes. Short-cut regenerated cellulose fibres were supplied by Lenzing in both crimped and uncrimped form. The fibres employed in the wetlaid process were all uncrimped whereas all airlaid fabrics were produced from crimped fibres to ensure process compatibility.

Table 3.1. Fibre specifications used to prepare experimental wet wipes

Fibre Type	Fibre length (mm)	Linear density (dtex)	Supplier
Lyocell (Tencel)	6, 8, 10	1.4, 1.7	Lenzing
Viscose	6, 8, 10	1.7	Lenzing
Wood pulp (Softwood craft)	2.06		Irving pulp & Paper
Wood pulp (Golden Isles Fluff Fully Treated - HA Grade 4822)	2.4		GP Cellulose LLC
Tencel A100	6, 8, 10	1.4	Lenzing
Tencel A300	8, 10	1.4	Lenzing
Tencel A300 (2)	8, 10	1.4	Lenzing

Golden isles™ fluff pulp was selected for its compatibility with the airlaid process (233, 234). It is Chemi-Thermo-Mechanical Fluff Pulp (CTMP), which provides excellent fibre separation during hammer milling and high absorption properties required for wipe applications. CTMP fibres are characterised as being coarser and stiffer than chemically treated pulp, with longer fibres and fewer fines, making them more suitable for the airlaid process (67). This is because the stiffer fibres disperse in air more effectively in the mixing chamber

of the airlay system and are therefore less likely to entangle prior to being deposited to form the web. Note that all the fibres utilised in this research were either natural cellulosics or man-made regenerated cellulose fibres. Therefore, even when the fibres were blended prior to web formation, the resulting fabrics were notionally of 100% cellulose composition, which is important to facilitate biodegradation after disposal. Blending of regenerated cellulose fibres with wood pulp also provides an established means of increasing the wet-strength of resultant fabrics in the wet state (58, 155).

Auxiliary chemicals in the form of a wet wipe lotion were utilised in the manufacture of wet wipe substrates. A commercially used Moist Toilet Tissue (MTT) lotion was supplied by Nice-Pak International, one of Europe's largest wet wipe manufacturers (Grade 104330).

3.2 Nonwoven fabric manufacture

Two principal nonwoven fabric manufacturing processes were utilised, both of which reflect commercial practice. The first involved short fibre airlaying (drylaid) followed by hydroentanglement and the second, wetlaying (wetlaid) followed by hydroentanglement.

3.2.1 Wetlaid fabric formation

Wetlaid fabrics are relatively dense, lightweight fabrics composed of short fibres formed using a modified paper making process. They are produced from highly dilute slurry of fibres suspended in water that is drained through a permeable screen, upon which the fibres are deposited in the form of a web.

Fabric density, overall cellulose content and the fibre length largely govern the difference between paper and wetlaid fabric formation. According to an EDANA definition (235) a wetlaid nonwoven can distinguished from paper when: *'more than 50% by mass of its fibrous content is made up of fibres (excluding chemically digested vegetable fibres) with a length to diameter ratio of greater than 300; or if the conditions in (a) do not apply then, if the following conditions are fulfilled: more than 30% by mass of its fibrous content is made up of fibres (excluding chemically digested vegetable fibres) with a length to diameter ratio greater than 300 and its density is less than 0.40 g.cm^{-3}.*

Wetlaid nonwoven production and papermaking both require the dispersion of fibres within an aqueous medium prior to forming a web. However, in the case of wetlaids, a much higher dilution factor (lower stock consistency) is utilised than in papermaking to ensure the fibres are effectively dispersed. The suspension of fibre in water, is then passed through an inclined wire, designed to increase hydraulic capacity, in which the majority of the water is removed and recycled leaving fibres deposited as a web on the wire. Bonding then takes place using hydrogen bonding, thermal bonding, mechanical bonding (typically hydroentangling) or by chemical (adhesive) bonding. A schematic of an inclined wire wetlaid former is shown in Figure 3.1.

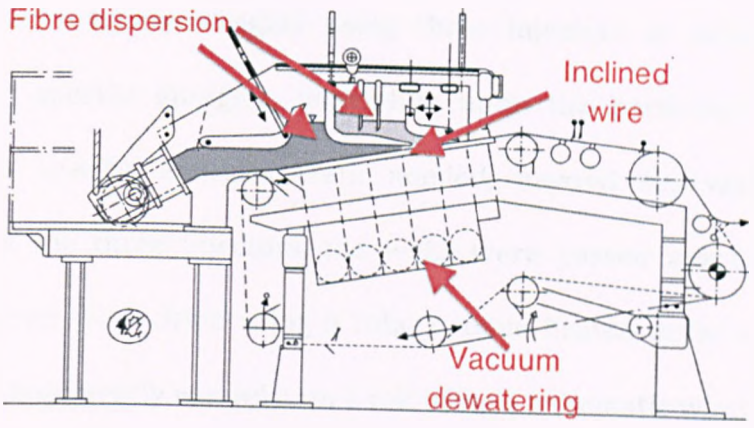
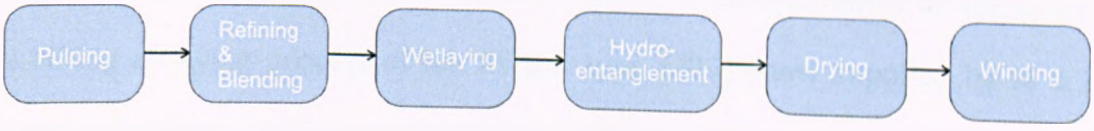


Figure 3.1. Twin layer inclined wire wetlaid former, adapted from Russell (236)

The wetlaid fabrics were produced using the systematic procedure given in Figure 3.2. The manufacture of the fabrics was intended to reflect commercial practice to ensure results were of wider relevance.



**Note that lotion was applied to the wipe substrates following drying and winding.*

Figure 3.2. Stages involved in the manufacture of experimental wetlaid substrates

The fabrics were made continuously on a 0.5 m wide pilot line at Windsor Locks (Ahlstrom, USA). The pilot line consists of refining and blending (fibre dispersion) capability before wetlaying on a single inclined wire former. The fibres were dispersed using a Hollander Beater. The substrate was formed on an incline paper machine set at a machine speed of 17 $m.min^{-1}$, targeting a basis weight of 60 $g.m^{-2}$.

The webs were hydroentangled using three injectors at various pressure profiles and specific energies, depending upon the particular experiment. Where high specific energies were needed, beyond the water pressure capacities of the three injectors, the webs were passed again through the process. Fabrics were dried using a rotary steam heated dryer at 180°C. The fabric was subsequently wound onto a roll using a pneumatic winding system.

3.2.2 Short-fibre airlaying

The short-fibre airlaid process originated as means to produce dry-laid paper but has evolved as major technology for the manufacture of nonwoven hygiene products and wipes. Short fibre airlaid fabrics for wipes are predominantly composed of fluff-pulp blended with man-made or natural fibres. In this study, a sifting airlaying process of the Kroyer type (237) (now supplied by M & J Airlaid Products A/S), was employed suitable for processing short fibres (2-12 mm). A schematic of the process is given in Figure 3.3.

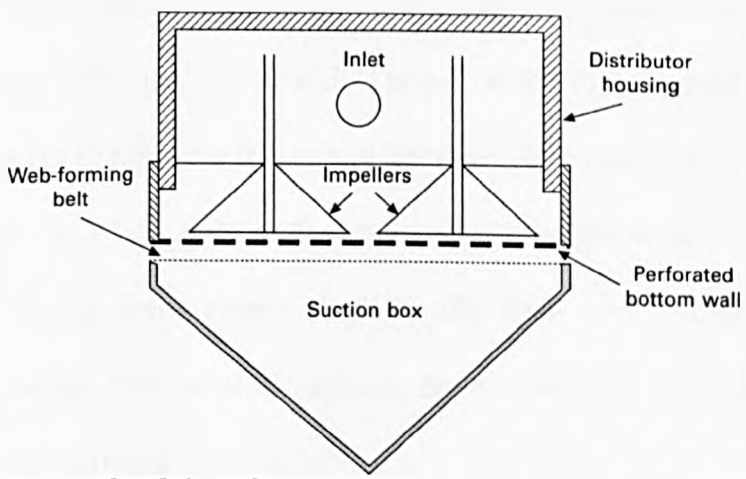


Figure 3.3. Schematic of the sifting airlaying process, adapted from Rasmussen (238)

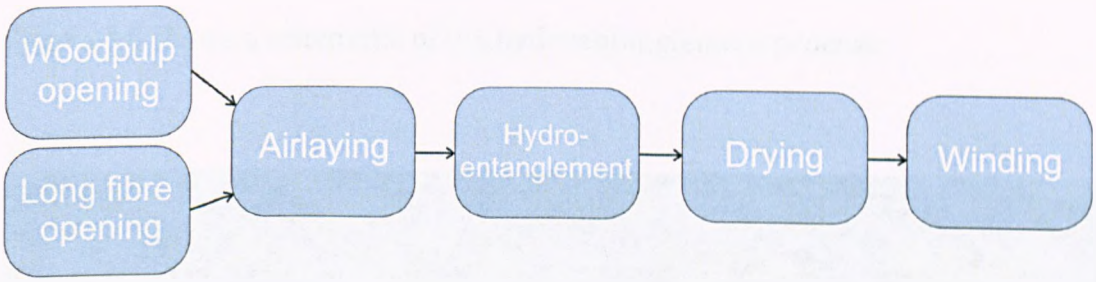
A turbulent airstream is maintained within the distributor housing (upper chamber) by means of rapidly rotating impellers using a rotational speed in this work of 1110 $r.min^{-1}$. The air turbulence serves to maintain separation of the fibres and their suspension, preventing agglomeration. As the fibres descend toward the perforated wall at the bottom, they are screened through a square metal grid (6 mm x 6 mm, 0.85 mm wire diameter), which helps to ensure only dispersed fibres are incorporated in to the web below. Fibres that pass through this grid are deposited on to a foraminous conveyor or belt assisted by a vacuum beneath. Resulting airlaid webs are roughly isotropic in terms of fibre orientation. Further details of the system utilised to make the webs have been reported by Osman (239).

Defibrated fluffpulp (Golden Isles Fluff™ Fully Treated - HA Grade 4822) was initially opened using a Hosokawa Alpine Rotoplex Granulator Ro 20/12 fitted with a 1.5 mm screen, and further opened using a small mechanical opener (Shirley F102/A Trash Analyzer) to reduce the nit content. The regenerated cellulose fibres (Viscose and lyocell/Tencel) were first passed through the airlaying process to open the fibres and improve fibre separation prior to being blended with the wood pulp in the appropriate weight ratio. Subsequently, these fibre blends were airlaid to form the final web using a stationary conveyor to reduce structural variation in the formed web. The airlaid machine settings are summarised in Table 3.2.

Table 3.2. Machine parameters for airlaid webs

Machine Parameters	Settings
Air velocity suction	1.7 $m.s^{-1}$
Screen aperture size	6 mm square mesh, 0.85 mm wire diameter
Conveyor belt	0.4 mm pore size, 0.23 mm wire diameter
Rotor blade dimension and speed	2 x 160 mm, 1100 $r.min^{-1}$
Rotor blade type	Narrow plate

The basic process steps used to produce the airlaid fabrics are summarised in Figure 3.4.



**Note that lotion was applied to the wipe substrates following drying and winding.*

Figure 3.4. Process steps for the formation of experimental airlaid wet wipe substrates*

To manufacture each small sample, 13g of opened regenerated cellulose fibre and wood pulp fibres in the required proportion were blended together by hand and then airlaid using the airlaying process. The conveyor speed was set to zero and all fibre collected upon a 70 mesh (0.212 mm openings) screen, which was placed onto the foraminous conveyor within the chamber. This method enabled complete removal of the mesh and transfer to hydroentanglement without disturbing the delicate web structure.

3.2.3 Hydroentanglement

Primary bonding of the airlaid webs was conducted using a 0.5 m wide hydroentangling pilot-line (STL Hydrolace), the basic configuration of which is illustrated in Figure 3.5. This unit consists of seven injectors. High-velocity, columnar, constricted water jets interact with fibres in the web and the support surface (the conveyor) resulting in fibre entanglements and displacements. In some cases, depending upon the fibre types being processed, the high impact forces and specific energies employed can cause longitudinal splitting of microfibrillar fibres (fibrillation) such as natural cellulosics and lyocell (236). Figure 3.6 shows a schematic of the hydroentanglement process.

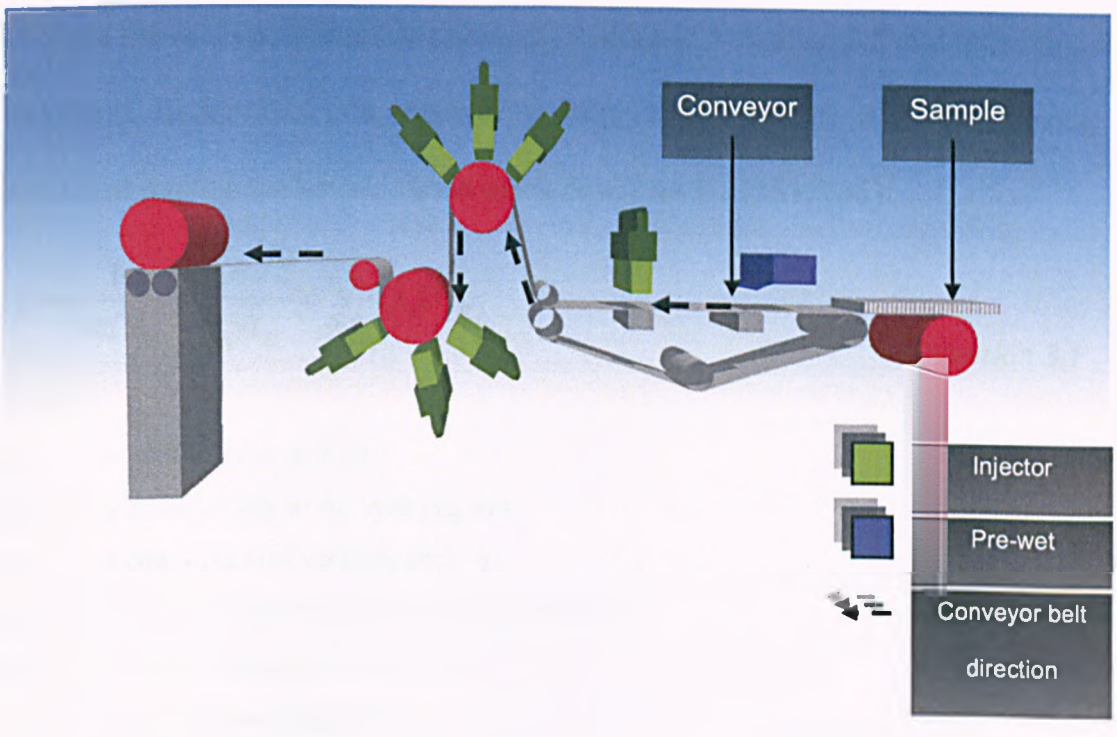


Figure 3.5. Schematic of the pilot hydroentangling system (240)

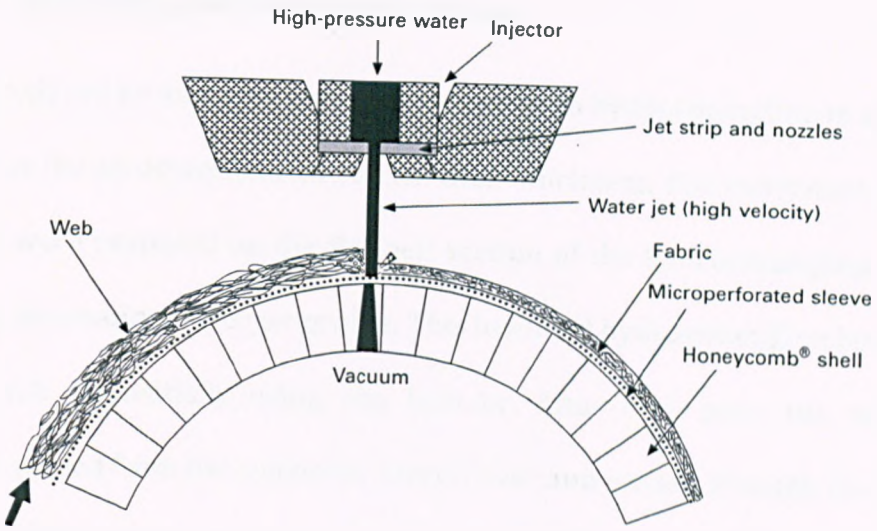


Figure 3.6. Schematic of the hydroentanglement process (236)

The resultant fabric properties after hydroentanglement are influenced by the specific energy introduced to the web. The specific energy consumed by a unit mass of fibres is dependent on the water pressure, flow rate and residence time of fibres under the jets. Specific energy K, ($J.kg^{-1}$) in the web during hydroentangling can be calculated using equation 3.1 (151, 236):

$$K = \frac{1}{bmV_b} \times \frac{C_d \delta \sqrt{2}}{4\sqrt{\rho_w}} \times \sum_{i=1}^{M} n_i l_i D_i^2 p_i^{3/2}$$

Equation 3.1

Where:

b = width of the web (m)

m = area density of the web ($kg.m^{-2}$)

V_b = conveyor belt velocity ($m.s^{-1}$)

p_i = water jet pressure at the i_{th} injector (Pa)

C_d = nozzle discharge coefficient

ρ_w = water density ($kg.m^{-3}$)

n_i = number of water jets on the i_{th} injector (per m)

l_i = width of i_{th} injector (m)

D_i = diameter of water jet nozzles in the i_{th} injector (m).

M = number of injectors (n)

3.2.3.1 Hydroentanglement of airlaid webs

Webs produced by airlaying were pre-wet prior to hydroentangling to evacuate air within the structure and to reduce their thickness. For convenience small samples were prepared on the flat belt section of the hydroentangling system using an alternating water jet profile. This involved hydroentangling both sides of the web sequentially using one injector. After each pass, the web was carefully peeled from the conveyor, turned over and passed through the system, such that the required alternating water jet profile could be obtained. All airlaid samples were produced using the same jet strips with 120 μm hole diameter and 1667 holes per metre. The water pressures or specific energies utilised varied according to the experiment and these values are reported in the individual experimental results sections. The jet pressures were kept below 50 bar due to the introduction of major disturbances in the web structure at higher pressures.

Hydroentangling conditions and fabric constructions utilised in the production of experimental wipe samples were selected to reflect as near as possible, those that could be adopted in industrial practice. Note that the fabrics produced were all based on blends of wood pulp and regenerated cellulose fibre; specific details of each blend are reported in the individual experimental results sections. Specific energies used in the production of the fabrics used in this research ranged from ca. 0.213 – 6.85 $MJ.kg^{-1}$. The water jet profile and line speeds are given in Table 3.3. All airlaid fabrics were hydroentangled on a 70 mesh conveyor (open area 33.8%), except where the influence of mesh size was investigated, whereby the mesh size was varied between 30-120 mesh.

Table 3.3. Hydroentanglement process conditions for experimental airlaid materials*

Specific Energy ($MJ.kg^{-1}$)	Water jet profile (bar)	Line speed ($m.min^{-1}$)
0.213	↓40	20
0.72	↓40 ↑40 ↓40	20
0.769	↓25 ↑25 ↓40 ↑40 ↓40	25
0.95	↓40 ↑40 ↓40 ↑40	20
1.192	↓40 ↑40 ↓40 ↑40 ↓40	20
5.52	↓25 ↑25 ↓40 ↑40 ↓50 ↑50	5
6.85	↓25 ↑25 ↓40 ↑40 ↓50 ↑50 ↓50	5

**arrows denote the direction of hydroentanglement relative to the fabric face*

After hydroentanglement fabrics were dried in a through-air oven at 130°C for 300 s.

3.2.3.2 Hydroentanglement of wetlaid webs

The wetlaid webs were already wetted-out as they exited the forming section and did not require pre-wetting. The formed webs were processed through three injectors, each was fitted with a jet strip having 790 holes per metre with an orifice diameter of 92 μm. Initial experiments used injector pressures of 13.8 bar, 20.7 bar and 20.7 bar, line speed 17 $m.min^{-1}$ yielding total specific energy of 0.213 $MJ.kg^{-1}$. Later experiments with higher inputted specific energy were achieved by reducing overall processing speed below 17 $m.min^{-1}$. The web was entangled on one face only whilst being supported by a 92 mesh (0.172 mm openings) wetlaid forming wire from Albany International. The hydroentangled

substrates were subsequently dried on a rotary steam heated dryer pressurised with 6.89 bar (100 PSI) of steam.

3.2.4 Impregnation of wetting liquid onto wipe substrate

A wetting liquid (lotion) is applied to wipe substrates to increase dirt removal performance from a surface being wiped. It has been observed that when particles are combined with liquid, their removal efficiency from a surface is much improved (241). Koh (242) observed that the wetting liquid acts as a transport medium for dirt particles aiding penetration and retention into the wipe structure.

Adult MTT is currently the most dominant application for flushable wipes, accounting for 55% of the overall market by volume (8). For this reason an industrial lotion designed for MTT applications was employed throughout this work (Grade 104330, supplied by Nice-Pak International). The lotion pH was 5.4. The composition is given in Table 3.4.

Table 3.4. Composition of industrial MTT lotion (Grade 104330) used as the wetting lotion

Ingredient	Proportion (%)
Deionised Water	97.685
Amphoteric surfactant	0.25
Humectant	0.5
Non-ionic surfactant	0.5
Preservative	0.88
pH buffer (Sodium Citrate)	0.08
pH buffer (Citric Acid)	0.005
Fragrance	0.1

Impregnation of the wipes with the wetting liquid was achieved using a Xiamen Rapid Company mangle applicator, a schematic representation is shown in Figure 3.7.

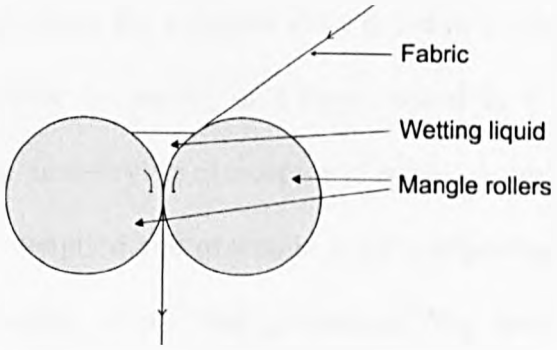


Figure 3.7. Schematic representation of mangle applicator used for applying MTT lotion

The MTT lotion was applied between the rubber coated rollers set at a nip pressure of 1 bar at a speed of 1 $m.min^{-1}$. The nonwoven was passed through the wetting liquid and through the nip with a resultant wet pick up between 300-350% w/w, as observed in commercial wet wipes. The impregnated wipes were stored in a sealed plastic bag to prevent evaporation and tested within 30 minutes of lotion application.

3.3 Analysis and testing methods

3.3.1 Dispersibility testing

The dispersibility of the nonwoven wipe samples was analysed using the INDA-EDANA tier 1 test, FG511.1 Dispersibility shake-flask test methodology (21). The test is designed to assess the physical breakup of a flushable product whilst being transported through sewage pumps and municipal wastewater conveyance systems (e.g. sewer pipes and lift stations). During the assessment

the pre-weighed dried wipes were placed in triple baffled flasks and subjected to orbital shaking.

For commercial wet wipes the samples were dried in a laboratory oven at 103 ±3°C for 4 hours prior to testing and then cooled in a desiccator prior to weighing to prevent post-drying atmospheric moisture uptake. Between 1-3 g of each sample was weighed and placed in a 2.8 L triple-baffled Fernbach flask with 1 L of tap water, as per the guidelines. Tap water was selected in preference to raw wastewater for reasons of laboratory hygiene and ease of supply. Deionised water is not recommended in the test as all waters contain dissolved salts so it does not represent real-world conditions. For completeness the shake-flask test was performed using deionised water with no observable difference in the results. The water used in these experiments had the specification shown in Table 3.5.

Table 3.5. Analysis of central Leeds mains water

Compound	Mean Level
Fluoride	0.076 mg.L-1
Aluminium	13.1 µg.L-1
Iron	22.45 µg.L-1
Manganese	2.77 µg.L-1
Nitrates (NO3)	7.59 mg.L-1
Chloride	25.7 mg.L-1

The flask was then placed on an orbital shaker (shown in Figure 3.8) with an orbit of 50 mm and rotated at 150 $r.min^{-1}$ for 6 hr. Each test was conducted in duplicate as a minimum, with a Whatman No.41 filter paper as a reference sample.

Figure 3.8. Shake-flask dispersibility test equipment, showing baffled flasks mounted on rotary shaker

The samples were then passed through a series of perforated stainless steel plate screens to assess the dispersibility of the material. The screen sizes were 12.5 mm, 6.3 mm, 3.15 mm and 1.6 mm. Using a handheld showerhead spray nozzle held approximately 15 cm above the screen the material was rinsed through the nested screens for 2 min at a flow rate of 4 $L.min^{-1}$ being careful not to force passage of the retained material through the next smaller screen. After rinsing, the top screen was removed and further rinsing was conducted on the next screen size down for t = 2 min. This was repeated until all screens had been rinsed. The retained material from each of the screens was removed using forceps.

Figure 3.9. 12.5 mm screen containing dispersed wipe residue after 6 hr.

Figure 3.9 shows an example of fibre retained on the 12.5 mm screen. The dry weight of the samples (initial and final) was determined by placing them in a tared aluminium weigh pan and drying them in an oven at 103±3°C for 4 hours. The samples were cooled in a desiccator prior to weighing to prevent post-drying atmospheric moisture uptake.

3.3.2 Fabric tensile properties

The dry and wet tensile strength of the fabrics was investigated through direct measurement using a tensile testing machine with a constant rate of extension. In the dry state the fabrics were conditioned in a standard atmosphere (243). Wet wipes were not conditioned before use and were tested in the wet state either directly from the pack (commercial wipes) or after impregnation with MTT lotion (experimental wipes). The wet pick-up was maintained between 300-400% on weight of fibre. The importance of wet strength relates to the conversion process wherein, fabrics are subject to tensile forces during their assembly in to the final wet wipe form, for example in winding and unwinding processes. Also, sufficient wet strength is required to ensure that their mechanical integrity is maintained during the use phase.

A modified version of the EDANA Strip Tensile Test WSP 110.4 (05) was employed with the gauge length reduced to 50 mm due to the small size of the commercial wipe samples. The rate of extension was 100 $mm.min^{-1}$ and the specimen width was reduced to 25 mm to enable more data to be obtained from the relative small experimental specimen sizes. Data was recorded in both the machine direction (MD) and cross direction (CD).

3.3.3 Measurement of fibrillation resistance (Canadian Standard Freeness method)

The measurement of Canadian Standard Freeness (CSF) is designed to give a measure of the rate at which a dilute suspension of pulp (3 g of pulp in 1 L of water) may be drained of water (244). It is widely used to assess the changes in drainage rate of chemical pulps during beating and refining, which increases the fineness and reduces the length of the wood fibres resulting in an increase in the amount of retained water. The higher the weight of retained water the lower the 'freeness' of the pulp. The method has also been used to assess the fibrillation resistance of Tencel fibres (245). Using this method, a reduction in CSF is observed if the fibre fibrillates.

The fibre moisture content was obtained gravimetrically after oven drying to constant weight at 110°C. 180 g (dry weight) of regenerated cellulose fibre was added to 18 kg of water to create a stock consistency of 1.0%. The stock was processed in a laboratory beater with a 23 L capacity using the following procedure:

- Fibre dispersed in water for 5 min.
- Beater roll housing raised to prevent clogging/fibre entanglement.
- Fibre circulated around the beater with the bed plate retracted (No beating) for 15 min to maximise dispersion.
- Initial stock sample taken (no beating).

- Beating was conducted for 60 min with stock samples taken every 15 min. A 7680 g beater bed plate counterweight was used during the beating cycle.
- After the first 15 min of beating the beater roller housing was lowered.

For each beaten stock sample the Canadian Standard Freeness was determined using a CSF tester, a schematic representation of the test equipment is shown in Figure 3.10.

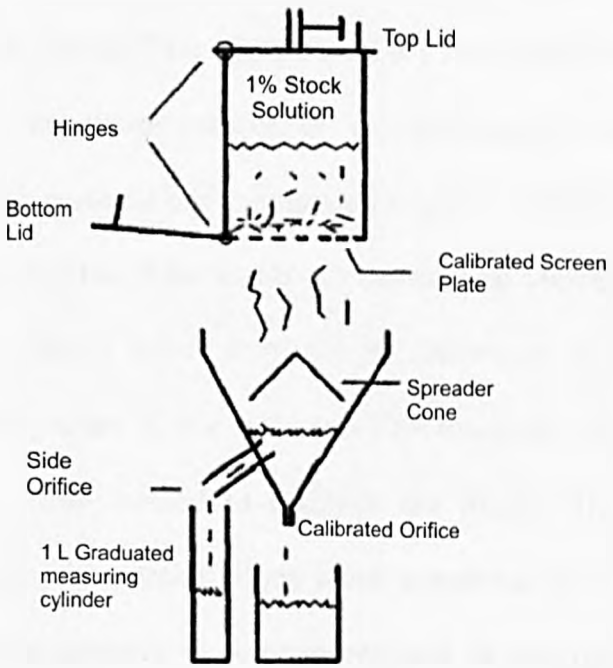


Figure 3.10. Schematic representation of CSF Tester, adapted from Biermann (246)

During the test, 1 L of stock solution was passed through the calibrated screen plate onto a spreader cone. If the water drains quickly it overflows through the side orifice and is collected in the graduated measuring cylinder. The CSF is the quantity (in ml) of water collected in the measuring cylinder.

3.3.4 Scanning Electron Microscopy

An analysis of the microstructure of the wipes was conducted on dry samples using both Camscan Series 4 and Jeol JSM-6610LV Scanning Electron Microscopes (SEM). The samples were prepared by sputter coating with a layer of gold. Magnification was varied between 50 – 1000 times.

3.3.5 Fibre composition analysis using ATR-FTIR

The chemical composition of commercially available wet wipes was analysed using Attenuated Total Reflectance (ATR) Fourier Transform Infra Red Spectroscopy (FTIR) (PerkinElmer Spectrum-BX FTIR). ATR-FTIR measures the material's absorption characteristics of electromagnetic radiation in the infrared region. Each material has a unique absorption profile corresponding to the vibrational frequencies of the material's constituent molecules. A typical IR spectrum has absorbance bands that can be attributed to the presence of individual chemical groups in the molecule. The resulting interferograms are added and Fourier transformed to produce the final FTIR spectrum. Test specimens from the commercial wipes were prepared for FTIR analysis by Soxhlet extraction in acetone to remove residual lotion and dried at room temperature.

3.3.6 X-ray Microtomography

X-ray Microtomography (XMT) operates using a similar principle to X-ray CT or CAT (Computed Axial Tomography) scanners found in hospitals, but has a spatial resolution that is typically hundreds or more times higher. The specimen is irradiated by a micro-focused-CT X-ray source and imaged onto a detector. A series of 2-D X-ray projections are acquired while rotating the

sample step by step through a full 360° cycle within the field of view at increments of less than 1° per step. The XMT machine collects multiple X-ray transmission images from different angular views, from which cross sections of the sample are reconstructed to provide a full 3D internal microstructure and density map. Figure 3.11 illustrates the operating principle of an XMT system.

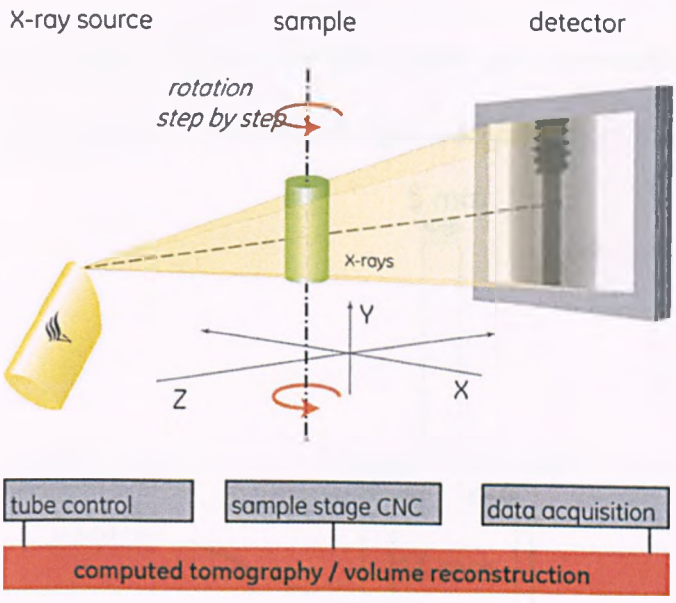


Figure 3.11. Schematic of a typical XMT system (247)

Fabrics for XMT analysis were prepared by pre-coating them with a 1M solution of iodine to improve the radio-contrast and dried at room temperature. The samples were then scanned using a Phoenix Nanotom XMT system, with a maximum pixel resolution of 0.5 µm. The images were rendered using VG Studio MAX 2.0 software (VolumeGraphics).

3.3.7 Fibre pull out test

A fibre pull-out test was devised to assess the relative sliding friction of regenerated cellulose fibres compared to lyocell. Previous attempts have been made removing single fibres from hydroentangled fabrics (248) but this

method was found to be impractical when dealing with short-fibre cellulosic materials. The modified approach taken measured the force required to remove a group of fibres in the form of a 5 mm wide tab at one end of the test specimen. The results of this test provide strong evidence of how the fabrics are likely to disassemble during dispersibility testing.

Specimens of 50 (height) x 20 mm (width) were prepared with a 5 mm wide tab at one end of the sample, as shown in Figure 3.12.

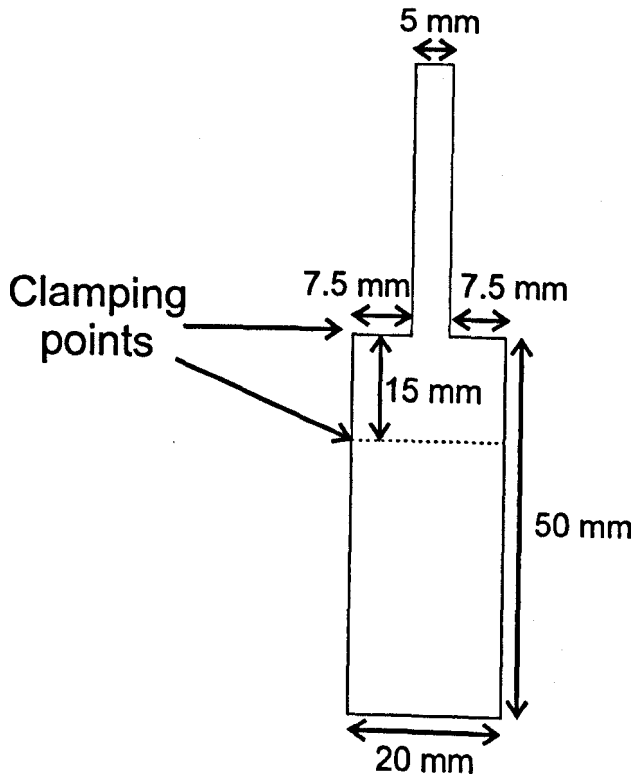


Figure 3.12. Specimen dimensions for fibre pull out test

Fabrics were tested in the dry and wet state. For wet state tests the fabrics were wetted with tap water to full absorbent capacity and allowed to drip dry for 2 min. The samples were clamped with the tab in the upper jaw of an extensometer. The other end of the specimen was clamped over its full width

with a gauge length of 15 mm. The force required to pull the fibres out of the fabric was measured at an extension rate of 25 $mm.min^{-1}$.

3.3.8 Thickness measurement

The dry thickness of commercial wipe samples was measured according to BS EN ISO 9073-2:1997 on a Rycobel ProGauge thickness tester appling 0.5 kPa over a test area of 25 cm^{-2}. The samples were prepared by gently rinsing in deionised water before drying at 103 ±3°C for 4 hours.

Chapter 4

Assessment of dispersion mechanisms in existing wipes

4.1 Introduction

To inform the experimental work on the development of wet wipe substrates it is instructive to understand the composition, structure, wet stability and dispersibility of existing products. Accordingly, a variety of commercially available wet wipe products were obtained with the primary aim of investigating their composition and structure as well as quantitatively determining their dry and wet strengths and their dispersibility in water, using standard methods. Each of these substrates is claimed to be flushable by their respective suppliers. Based on this data it was possible to identify the basic mechanisms that each relied upon to enable them to be described as 'flushable'.

4.2 Selection of commercial wet wipe substrates

Five market-leading wet wipe products were commercially sourced, details of which are given in Table 4.1. These products were selected because they are representative of those utilised in Europe, the USA and Japan, where the majority of flushable wipes are consumed. Wipes from different product categories were investigated to identify if different end-uses affected the fabric design. These include Moist Toilet Tissue (MTT), Toddler wipes and Bathroom

cleaning wipes. All commercial wipes were supplied loaded with the wetting lotion. The samples were gently rinsed in deionised water before drying at 103 ±3°C for 4 hours but residual components of the lotion could still be present. For this reason, the dry weights given in Table 4.1 should be considered approximate values.

Table 4.1. Details of commercial wet wipe samples

Brand	Application	Manufacturer, Technology	Thickness (mm), CV (%)	Wet Areal Density ($g.m^{-2}$), CV (%)	Dry Areal Density ($g.m^{-2}$), CV (%)	Lotion Add-on (%), CV(%)	Sample Reference
Carrefour	MTT	Suominen, wetlaid hydroentangled	0.494, 5.13	214.83, 3.70	58.64, 2.89	367, 4.94	CAR01
Andrex	MTT	Kimberly Clark, Airlaid chemical bonded	0.540, 14.13	238.89, 3.95	76.19, 8.21	315, 6.17	AND01
Japanese branded	Toddler	Unicharm, wetlaid hydroentangled	0.348, 5.80	184.18, 2.23	51.82, 2.31	356, 3.44	UNI01
Pampers Kandoo	Toddler	Proctor & Gamble, Carded hydroentangled	0.617, 4.39	188.61, 4.64	54.87, 4.97	344, 5.40	KAN01
Jeyes Parozone	Bathroom cleaning	Unknown, Airlaid chemical bonded	0.634, 8.67	211.81, 3.56	68.26, 2.49	310, 3.84	PAR01

The lotion add-on was calculated from the measured dry weight compared to the wet weight taken immediately after removal from the wet wipe pack. As residual components of the lotion could still be present the wet weights should be considered as approximate values.

The substrates utilised in each product were produced by different manufacturing methods. The Kandoo (KAN01), Parozone (PAR01) and Andrex (AND01) wipes were manufactured using airlaid web formation and chemical bonding. The Andrex wipes were manufactured in the USA using Kimberly Clarks' ion-triggerable binder technology, described in section 2.7.3.1. The wipes manufactured by Unicharm (UNI01) in Japan and Suominen (CAR01) in France and the USA were produced by wetlaying and hydroentanglement.

Areal densities for the commercial wipe substrates were between 51-76 $g.m^{-2}$ and thicknesses between 0.348 mm and 0.634 mm. The wipes manufactured on airlaid platforms were of higher thickness than the wetlaid substrates of comparable basis weight. This may be expected since the hydraulic forces imparted to the fibres during laydown in wetlaying can be expected to lead to greater compaction of the structure than in airlaying. Additionally, since the wetlaid wipes were mechanically bonded using hydroentanglement, further reduction in thickness with increasing web consolidation would be anticipated. The lotion wet pick-up varied between 300-367% w/w.

An analysis of each substrate was completed to understand the composition and structure of the fabric. FTIR spectroscopy was conducted to identify the

chemical components of the wipes and scanning electron microscopy was employed to understand the microstructural architecture of the wipes. The wet tensile strength and dispersibility were measured to understand the current state of the art in flushable wipes and provide a benchmark for a redesigned flushable wiping substrate. The wet wipes were removed from the pack subjected to soxhlet extraction in acetone for 20 minutes to remove the lotion. The samples were subsequently dried in a laboratory oven at 60°C for 2 hr before being subjected to ATR-FTIR and SEM analysis. The wet tensile strength and dispersibility of the materials was assessed using the methodology given in sections 3.3.1 and 3.3.2.

4.3 Results of the ATR-FTIR analysis

The chemical composition of a wipe plays an important role in its flushability performance. The constituent materials can influence biodegradability as well as dispersibility and wet strength. To identify the composition of the commercial flushable wipes Attenuated Total Reflectance Fourier Transform Infra Red Spectroscopy (ATR-FTIR) analysis was performed using the methodology provided in 3.3.5. Examples of spectra for the commercial wipe substrates are given in Figure 4.1 to Figure 4.5

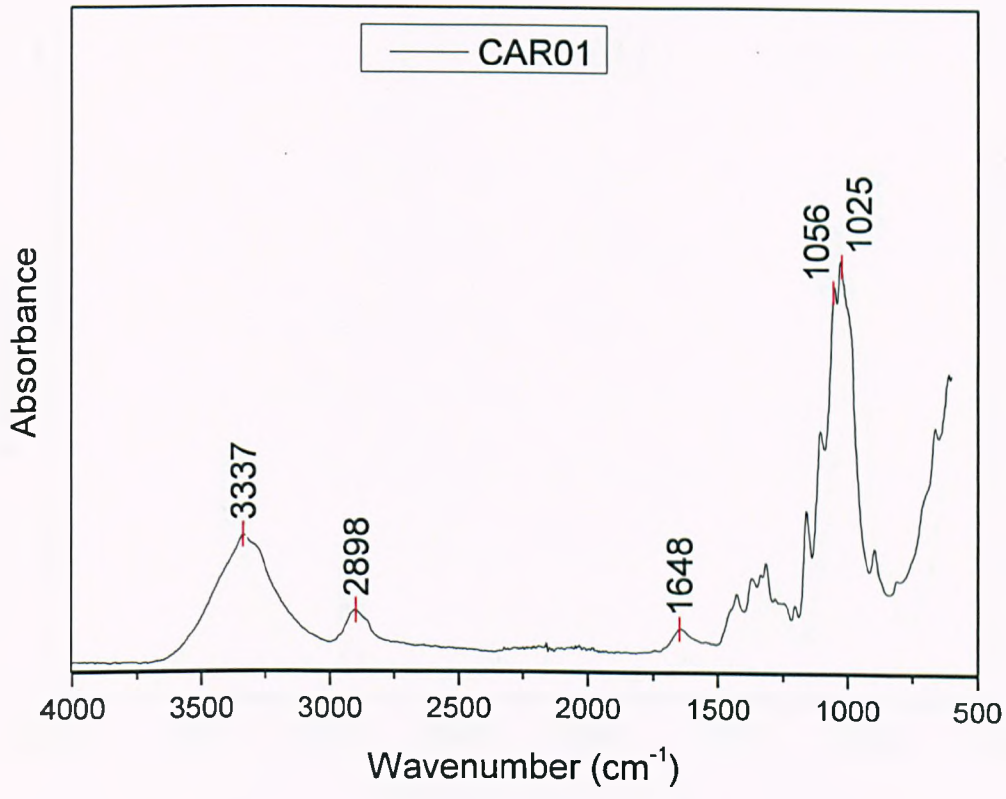


Figure 4.1. FTIR spectrograph for CAR01

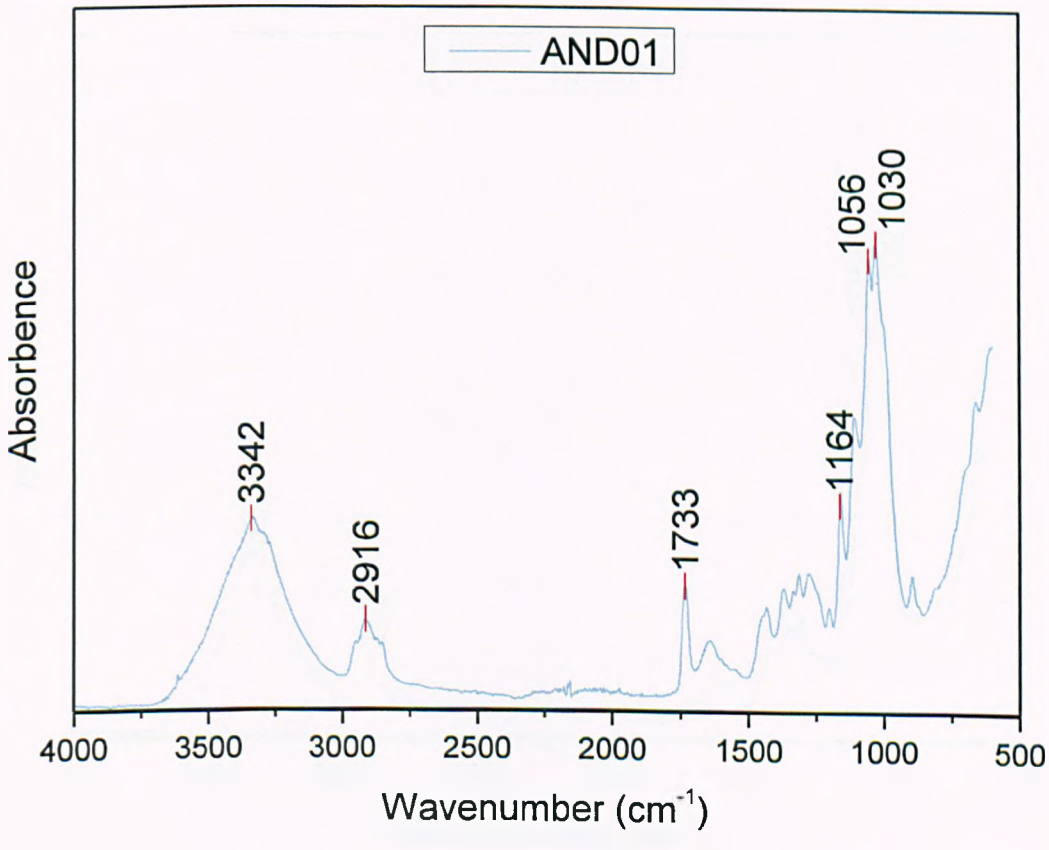


Figure 4.2. FTIR spectrograph for AND01

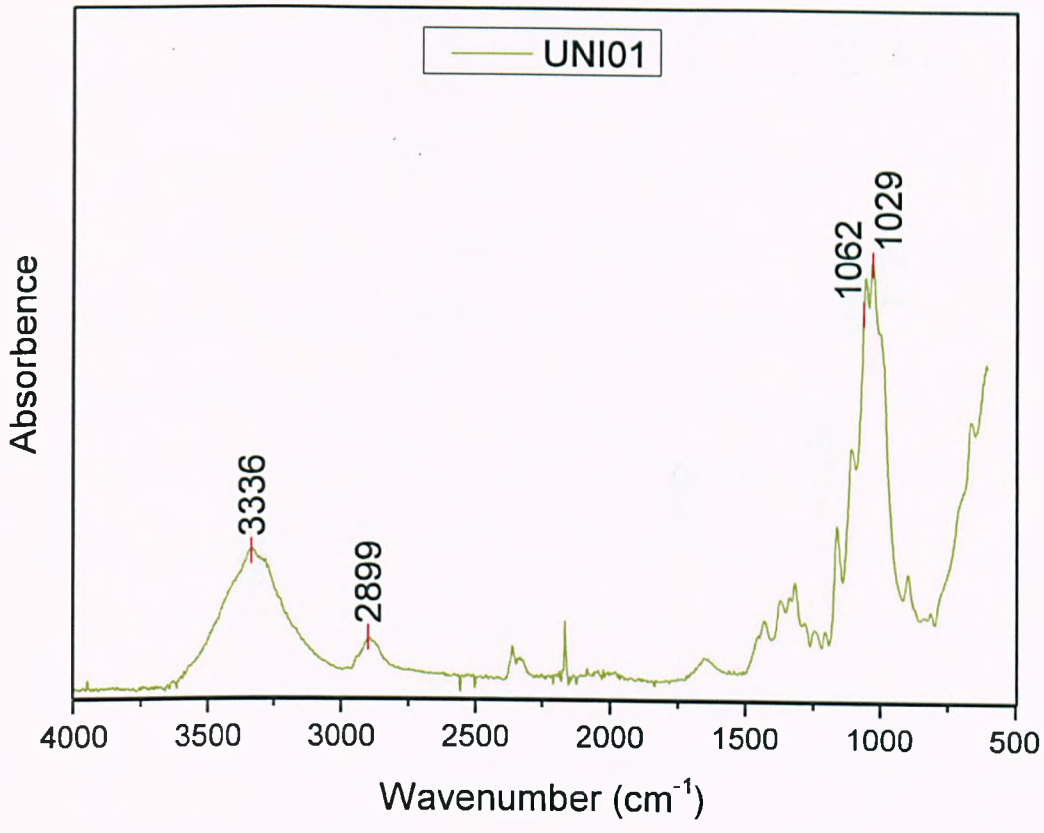


Figure 4.3. FTIR spectrograph for UNI01

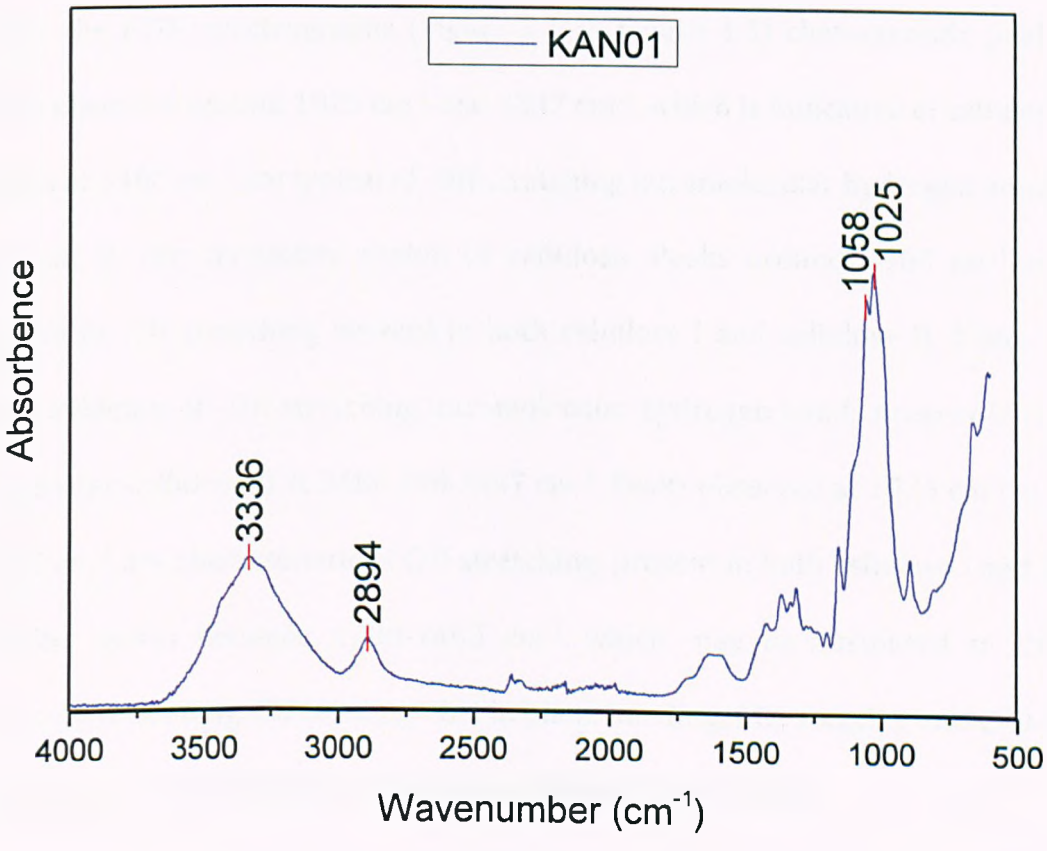


Figure 4.4. FTIR spectrograph for KAN01

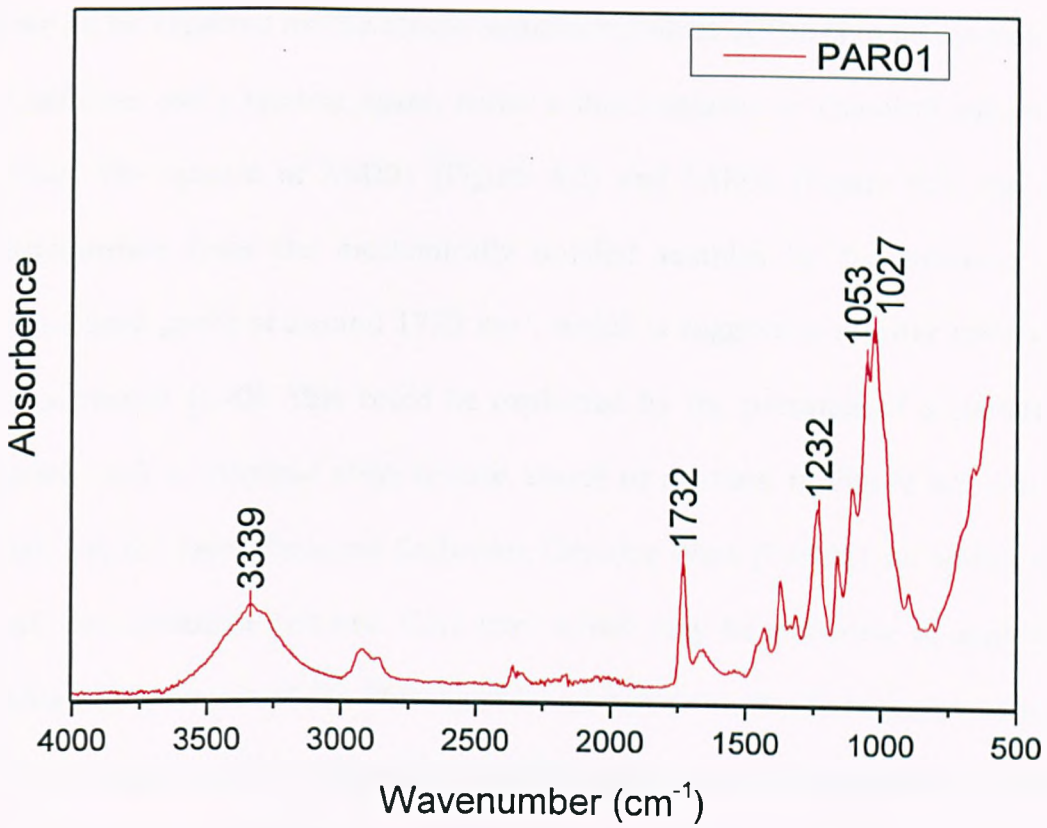


Figure 4.5. FTIR spectrograph for PAR01

In all the FTIR spectrographs (Figure 4.1 to Figure 4.5) characteristic peaks were observed around 1025 cm^{-1} and 3337 cm^{-1}, which is indicative of cellulose. Peaks at 3300 cm^{-1} are typical of -OH stretching intramolecular hydrogen bonds present in the crystalline region of cellulose. Peaks around 2900 cm^{-1} are typical of -CH stretching present in both cellulose I and cellulose II. There is little evidence of –OH stretching intramolecular hydrogen bonds present in the crystalline cellulose II at 3488 and 3447 cm^{-1}. Peaks observed at 1035 cm^{-1} and 1055 cm^{-1} are characteristic of C-0 stretching, present in both cellulose I and II. Smaller peaks between 1200-1400 cm^{-1}, which may be attributed to CH_2 symmetric bending, CH bending –OH in plane bending, CH_2 wagging and C–O–C asymmetric stretching present in both cellulose I and II (249).

It would be expected for the airlaid materials (PAR01, AND01) to be composed of cellulose and a binding agent, either a thermoplastic or chemical adhesive binder. The spectra of AND01 (Figure 4.2) and PAR01 (Figure 4.5) can be distinguished from the mechanically bonded samples by the presence of pronounced peaks at around 1733 cm^{-1}, which is suggestive of ester carbonyl group stretch (C=O). This could be explained by the presence of a chemical binder, such as ethylene vinyl acetate, starch or alginate. In Figure 4.5, which relates to the Jeyes Parozone Bathroom Cleaning Wipe (PAR01), an additional peak was identified between 1232 cm^{-1}, which may be indicative of aliphatic amine group stretch (C-N). This could be an acrylic binder formulation, which are commonly used in chemically bonded nonwovens. As discussed in section 2.7.3.6 one of the approaches to increasing the wet strength of wet wipe substrates is the use of an adhesive binder, and so the presence of a synthetic binder in this sample can be explained in these terms.

The presence of cellulose in all the commercial wipes substrates is not surprising given that wood pulp is known to be one of the most common constituents due to its hydrophilicity, low cost and short fibre length. Further SEM investigation was conducted to understand if a blend of cellulose I (e.g. wood pulp) and cellulose II (e.g. regenerated cellulose) was used to produce the wipe substrates.

4.4 Results of the SEM analysis on commercial wipe fabrics

In addition to enabling the morphology of the fibre compositions in the fabric to be observed, SEM analysis also assisted in determining the nature of fibre entanglement and the microstructure of the commercial wipe structures. Analysing the fabric microstructure and fibre morphology before and after dispersibility testing also provided important insights into the mechanisms of dispersion of the fabric in water.

Samples for the SEM work were prepared using the methodology set out in section 3.3.4. The wet wipes were removed straight from the pack, washed with acetone to remove the lotion and then dried in a laboratory oven at 103°C for 4 hr before sputter coating. Five specimens per sample were prepared to prevent analysis of anomalous regions. The specimens were observed at multiple magnifications, ranging from 50-1000 times.

Typical SEM micrographs of each of the commercial wipe substrates are given in Figure 4.6 to Figure 4.10 show the original microstructure of the commercial wipes after being removed from the pack as well as after dispersibility testing in the shake flask.

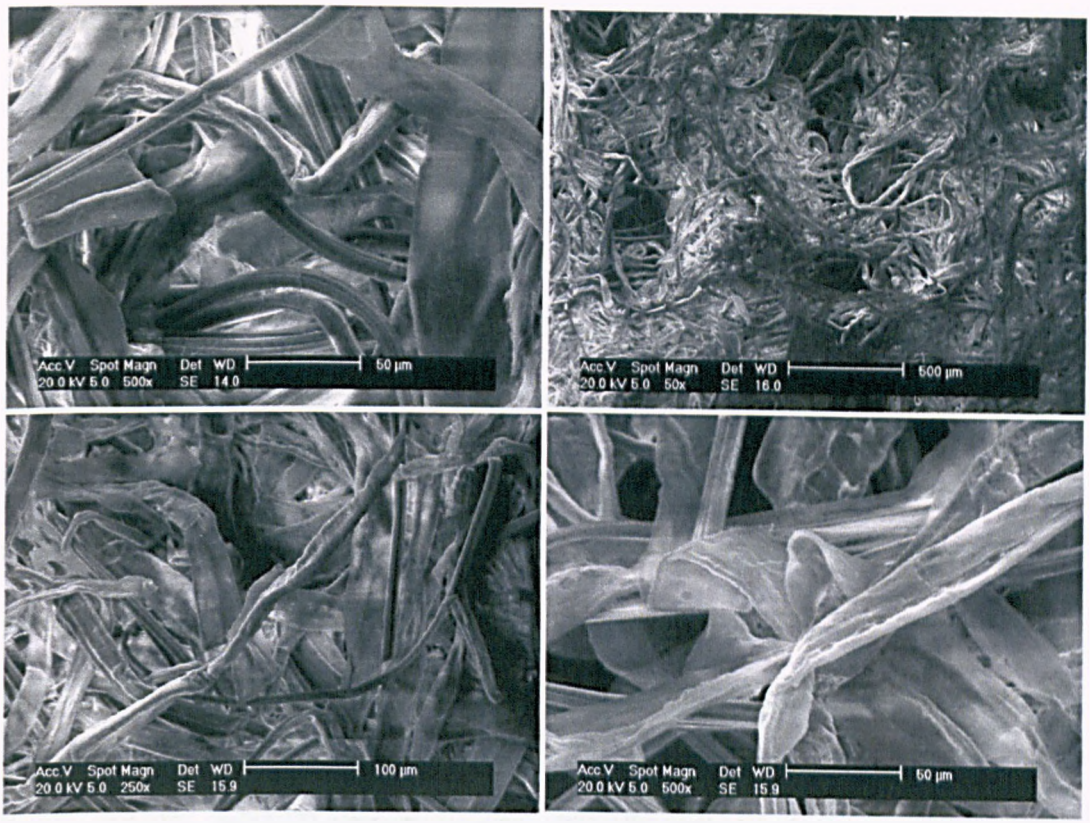


Figure 4.6. SEM micrographs of the UNI01 wipe substrate

The SEM images of UNI01 (Figure 4.6) reveal flat, ribbon-like fibres, with varied diameters up to 50 µm, which are entirely characteristic of wood pulp. There is also evidence of a second fibre present in lower numerical proportion with a nearly invariant diameter of about 12 µm. The second fibre component has an approximate circular cross-section and a striated surface along the axis, which is characteristic of the regenerated cellulose fibre, viscose. Thus, fibres comprising of cellulose I and II were found in UNI01. No chemical binder residues bridging the fibre surfaces were observed and the twisted and looped configuration of the fibre ends was highly suggestive of mechanical bonding via hydroentanglement.

The wood pulp content appears to be high compared to the viscose. Consequently, because the substrate is reliant on mechanical bonding of very short pulp fibres of relatively large diameter (~50 μm), the fabric wet strength of wipe UNI01 can be expected to be relatively low. This is also reflected by previous studies of hydroentangled wood pulp fabrics (230). Note that in structures such as these it is possible that hydrogen bonding will contribute to the network strength where the fibres are in direct contact. However, such interfacial bonding is unlikely to be a major contribution to the overall wet strength when the substrate is impregnated with lotion.

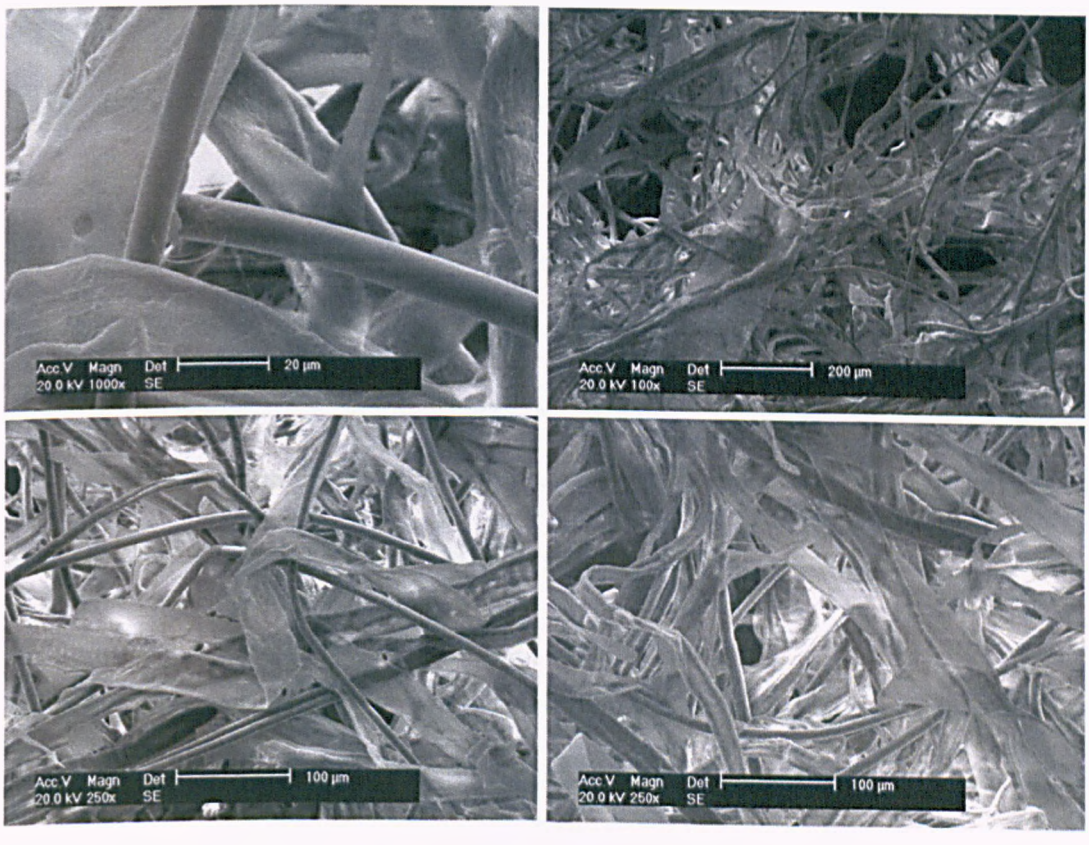


Figure 4.7. SEM micrographs of the CAR01 wipe substrate

In Figure 4.7 the SEM images of wipe CAR01 clearly indicate the presence of two different fibre types, one with a flat, ribbon-like structure consistent with wood pulp, similar to that observed in UNI01 and another with a round cross-

section and a smooth surface morphology. The latter component with round cross-section and a diameter of approximately 11 μm was known to be lyocell, which is based on regenerated cellulose pulp. Compared to other regenerated cellulose fibres such as viscose, the wet tenacity of lyocell is relatively high at 340-380 mN tex^{-1} (117) and this has been found to contribute to a high hydroentangled fabric wet strength (120). The SEM micrographs for the CAR01 sample reveal a network of fibres in which there is evidence of twisting and interlacing of adjacent fibres around their neighbours, particularly the lyocell fibres. This is consistent with the effect of hydroentanglement. It is known that at elevated hydroentangling pressure, at above approximately 100 bar, fibrillation of lyocell fibres can be induced (143). In the SEM images of CAR01, no evidence of fibrillation (longitudinal splitting of the fibre to reveal constituent fibrils) could be observed, suggesting that the fabric had been bonded at a relatively low hydroentangling pressure. This confirms both the presence of cellulose I and II in the substrate composition. As observed with wipe UNI01, no chemical binder, and twisted and looped fibre configurations suggests mechanical bonding via hydroentanglement.

Based on Figure 4.8, wipe AND01 was found to comprise a blended fibre composition of wood pulp and a smaller diameter (~11 μm) round cross-section fibre.

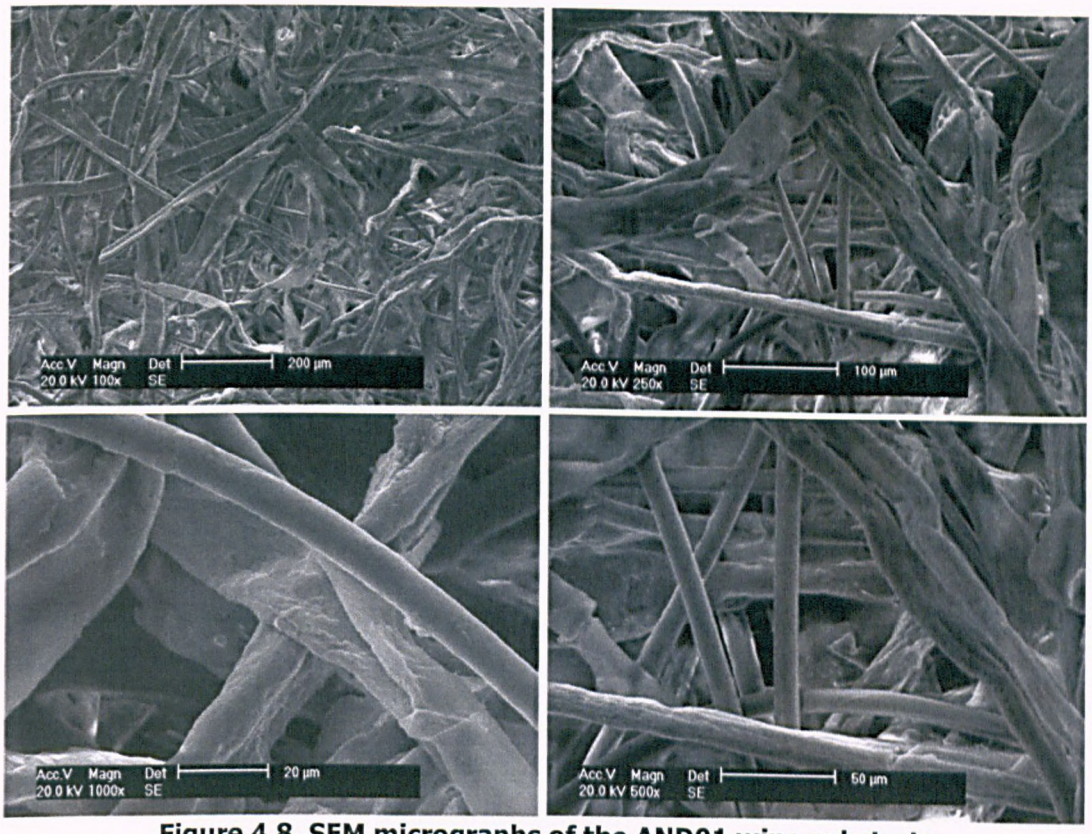


Figure 4.8. SEM micrographs of the AND01 wipe substrate

Given that the FTIR spectra (Figure 4.3) suggested that all the fibres were cellulosic in composition, approximately round fibre cross-sectioned fibre is likely to be lyocell. Additionally, evidence of the presence of a chemical binder was found indicated by the coated appearance of the constituent fibres and some film phase bridging of individual fibres, which can be expected to increase the wet strength of the entangled fibre network. The spectrum of this material showed pronounced peaks around 1733 cm^{-1}. This peak is suggestive of which is suggestive of ester carbonyl group stretch (C=O). This could be explained by the presence of a chemical binder, such as ethylene vinyl acetate (EVA), starch or alginate, materials commonly employed as binders. EVA is commonly used in wipe applications because it imparts high wet strength and hydrophilicity at a lower cost than acrylic binders (250), it also reduces binder viscosity and improves spray quality (179).

Based on the length of the fibres in the fabric (~10 mm), and the relatively low density (3.34 $kg.m^{-3}$), it was concluded that the fabric had been produced using airlaying and chemical bonding. This is plausible given that there is substantial installed capacity in industry producing wipe substrates using this route. In relation to this particular substrate, the literature suggests that the binder is triggerable (8, 251), i.e. its binding strength is dependent on the ionic strength of the surrounding liquid, or the lotion in this case. Of the mechanisms that have been identified by industry to impart dispersibility and adequate wet strength during use, delayed binder solvation has generated the most attention, particularly based upon the salting-out phenomenon (179). Although this in an effective approach, issues with divalent ion sensitivity can hinder solvation in hard water.

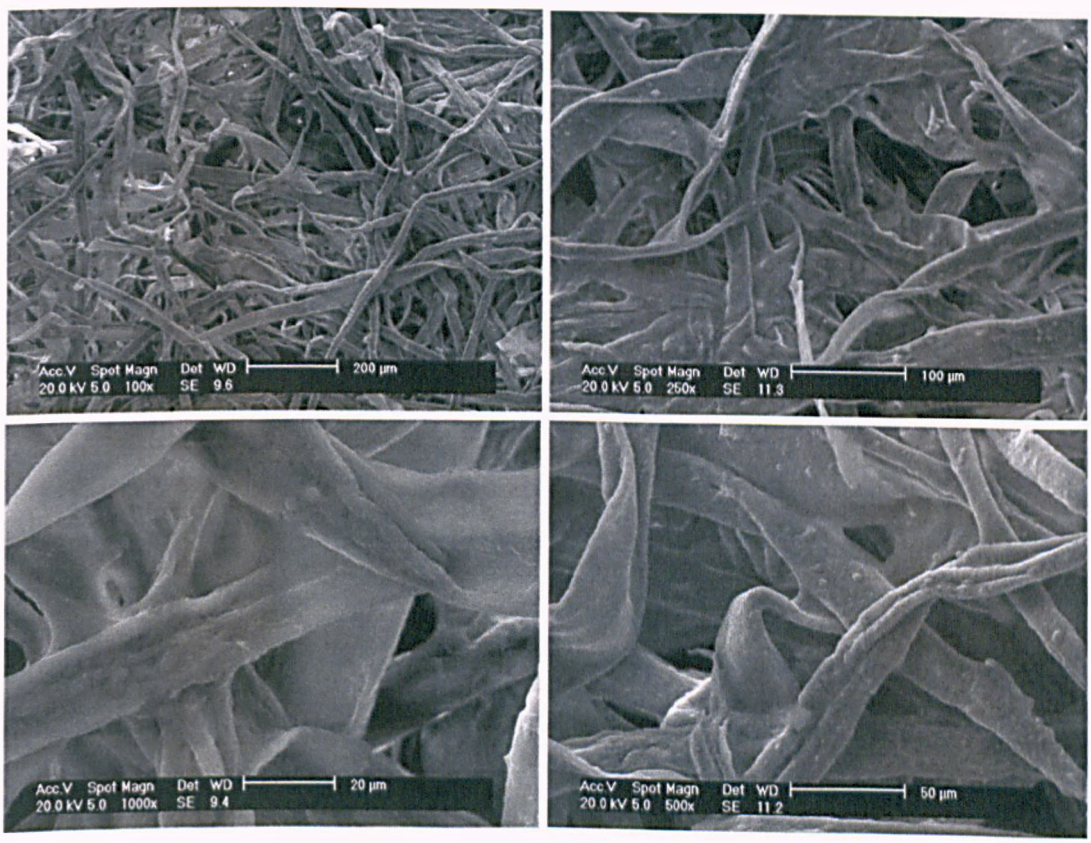


Figure 4.9. SEM micrographs of the PAR01 wipe substrate

In Figure 4.9 PAR01 appeared to be composed entirely of wood pulp fibre, with its characteristic flat ribbon-like structure. The film phase bridging individual fibres is indicative of an adhesive binder, and this film network was found to be more extensively distributed across the wipe structure compared to AND01. The FTIR peak (Figure 4.5) at 1232 cm^{-1}, which may be indicative of aliphatic amine group stretch (C-N). This could be an acrylic binder formulation, which are commonly used in airlaid wet wipes. There appears to be a high level of chemical binder present compared to AND01, which could be expected to have a high influence on wipe properties.

The SEM micrographs in Figure 4.10 indicate that wipe KAN01 comprised wood pulp and a man-made fibre with a round cross-section with a diameter of about 15 μm. Intensive fibre entanglement and the lack of an adhesive binder strongly suggests the fabric was hydroentangled.

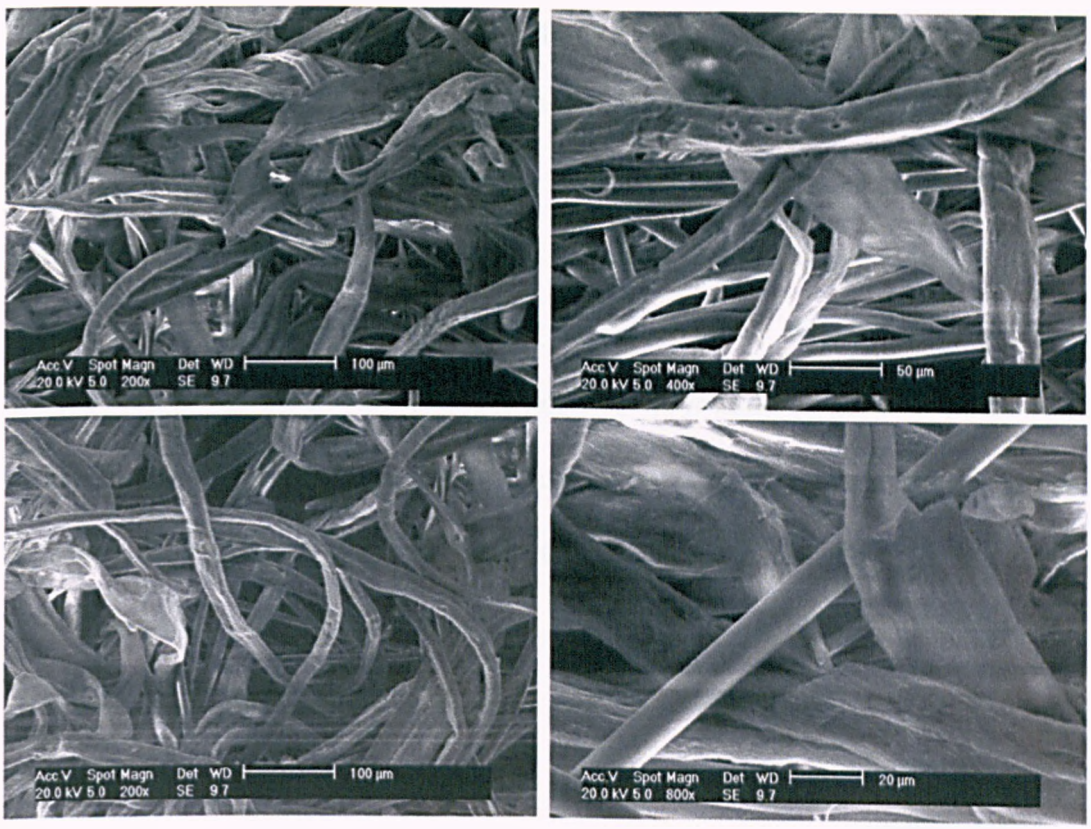


Figure 4.10. SEM micrographs of the KAN01 wipe substrate

The wipe comprises two very different lengths of fibre, wood pulp, which is very short (<3 mm) and a much longer man-made fibre of 40-45 mm in length. This particular combination, together with the looped configuration of the long fibre suggests that the wood pulp has been airlaid onto a carded base web, followed by hydroentangling to integrate the two layers together.

4.5 Wet tensile strength of commercial wipes

As discussed in section 2.5, the wet tensile strength of a wet wipe substrate is critical to ensuring it can be removed from the pack without breaking and remains in tact during use. Also, during converting processes fabrics are subjected to tensile forces during winding and unwinding operations and any

breakages leads to machine stoppages and other faults. Therefore, measurement of wet strength is of great importance both from the perspective of ensuring satisfactory performance during use and processing efficiency during manufacture. The wet tensile strength of the wipe substrates was determined using the procedure given in section 3.3.2. The wipes were tested straight out of the pack with a gauge length of 50 mm and a sample width of 25 mm, the extension rate was 100 mm.min^{-1}. The samples were measured in the machine direction (MD) and the cross direction (CD) and the results are shown in Figure 4.11.

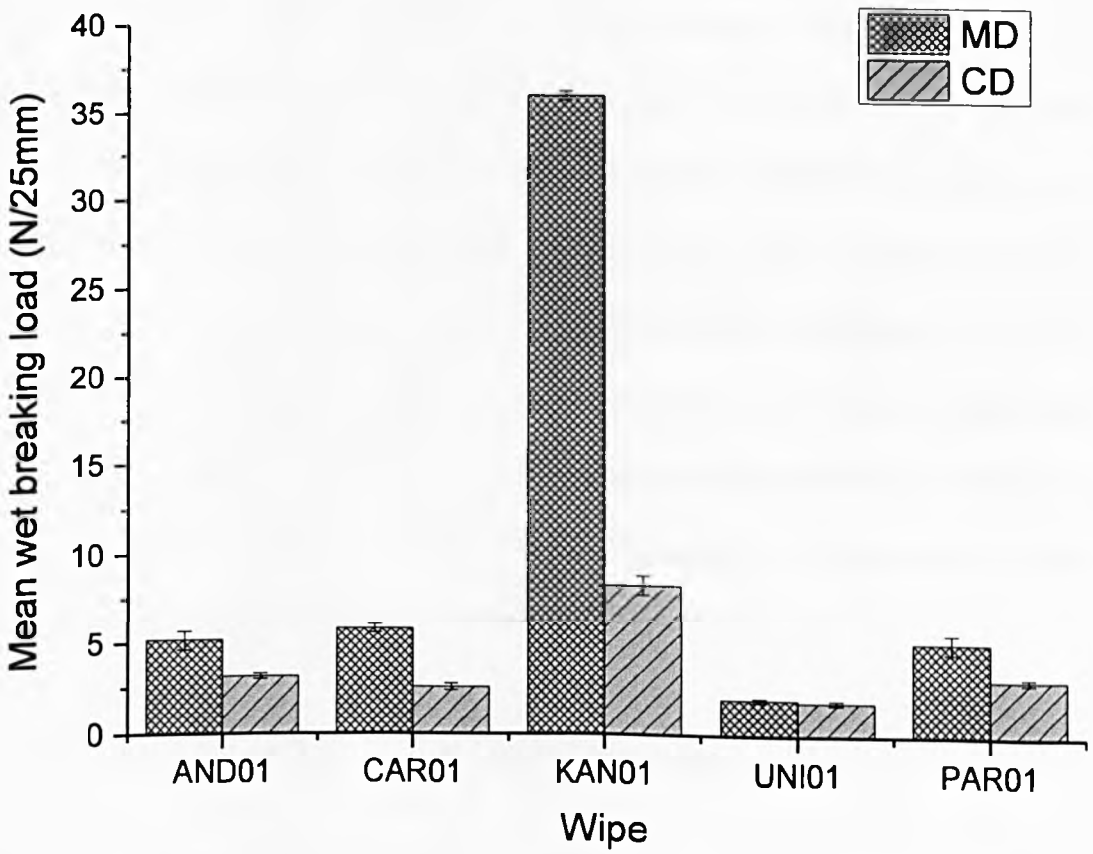


Figure 4.11. Wet tensile strength of commercial wet wipe samples; key is provided in Table 4.1

Figure 4.11 indicates that apart from the UNI01 sample, the wipes were consistently stronger in the machine direction (MD), clearly indicating anisotropy in the fabric structure. It is common in many nonwoven processes for the MD:CD ratio to be greater than 1 due to preferential fibre orientation, which is influenced by the way in which the fabric is manufactured. KAN01 exhibited the highest wet tensile strength amongst all the commercial flushable wipes, with the MD wet tensile strength being over seven times higher than the next strongest wipe. PAR01, CAR01 and AND01 yielded wet strengths of less than 5N/25 mm, which from a practical perspective would be on the threshold of acceptable strength for processing and functional use by the consumer. By contrast UNI01 exhibited very low wet tensile strength (<2N/25 mm), in both the MD and CD, but was the most isotropic with little difference between the MD and CD wet tensile strengths. With the exception of KAN01, all commercial wipes exhibit wet tensile strength below that of the aspirational specification stated in 2.9. The high wet tensile strength of KAN01 is surprising given that it is produced on an airlaid platform but the presence of a chemical binder can help explain the wet strength results. The dispersibility performance should be considered in conjunction with the wet strength to assess the overall performance of the wipe.

4.6 Commercial wipe dispersibility in water

The ability to disperse in an aqueous environment with mechanical agitation is an important requirement for compatibility with wastewater processes. If the wipe does not break up during transportation to the wastewater processing

plant, it can become snagged upon root-penetrated pipework and cause blockages. Filter screens at the entrance to the wastewater treatment plant filter out gross solids of greater than 6 mm^2, so it is imperative that the wipe disperses into smaller discrete elements before it enters the processing plant.

The commercial wipe samples were subjected to shake-flask agitation for 6 hours and the residual fibres washed through a series of graded screens, as detailed in section 3.3.1. Figure 4.12 shows the mean clearance of the commercial wet wipes through the graded screens, which provides an indication of the dispersibility of the substrates.

The degree of dispersibility, in terms of the residual particle sizes retained on the grids differed greatly between the samples. The dispersibility of standard toilet tissue (Andrex Classic White) is also included to provide a positive control reference since this is currently the only universally accepted flushable material. Note that 100% of the toilet tissue passed through all the screens (Figure 4.12), however, it should be noted that toilet tissue exhibits extremely low wet strength (<0.5 N/25 mm).

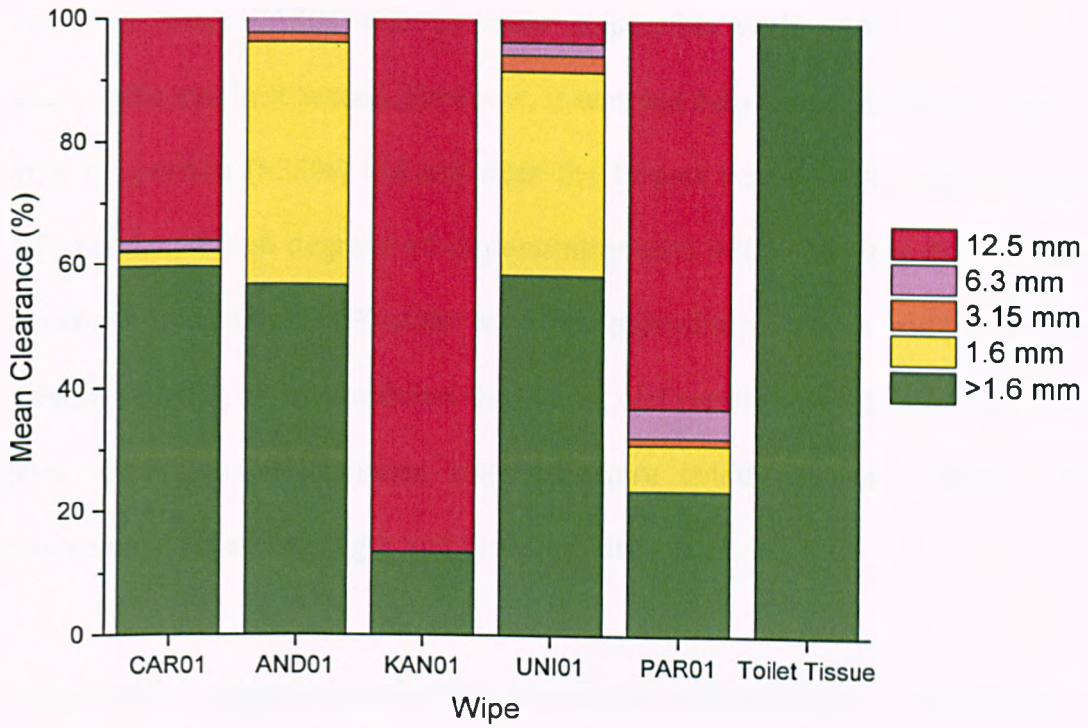


Figure 4.12. Mean clearance of commercial flushable products showing variable dispersibility

In Figure 4.12, all the nonwoven wipes samples produced lower mean clearance values than the reference toilet tissue. The KAN01 wipe did not break-up, with >85% of the weight of the wipe being retained by the largest screen of 12.5 mm. The relatively high tensile strength of the wipe KAN01 may also help to explain the poor dispersibility of the wipe observed in Figure 4.12. For 6.3 mm screen its dispersibility was very poor (13% mean clearance) suggesting that this product would not disintegrate sufficiently to enable it to pass through filter screens at a wastewater treatment plant and cannot be considered flushable.

PAR01 also did not disperse effectively, with approximately 63% of the wipe failing to clear the largest screen. Both KAN01 and PAR01 are characterised as largely staying intact with small particulates breaking off and clearing the

smaller screens. CAR01 was partially dispersible with >60% of the wipe clearing the smallest screen. However, it was not fully dispersible given that a large proportion (>35%) did not clear the largest screen. UNI01 and AND01 both produced high degrees of dispersibility with >90% clearing the 12.5mm screen. Approximately 60% of the wipe also passed through the smallest screen (1.6mm). UNI01, which exhibited the lowest wet tensile strength and relatively good dispersion performance suggests there could be some relationship between wet tensile strength and dispersibility.

This is further suggested by the data for sample CAR01 (Figure 4.11 and Figure 4.12), which possessed twice the MD wet strength of UNI01 but whose dispersibility value was 62% by weight (6.3 mm screen). However, it is simplistic to suggest that there will be a direct relationship between fabric strength and dispersibility because of the many ways in which wipe substrates are manufactured. For example, the AND01 sample exhibited similar wet tensile strength to the CAR01 sample but exhibited greater dispersibility (98% through 6.3 mm screen). Compared with UNI01, wipe PAR01 showed relatively high wet MD breaking load (10.32 N) but poor dispersibility, only 32% cleared the 6.3 mm screen. CAR01 exhibited modest dispersibility with 36% retained on the largest screen (12.5 mm) but this is almost double the clearance of PAR01 (63%). PAR01, CAR01 and AND01 show comparable wet tensile strength but different dispersibility performance.

Figure 4.13 helps to elucidate the relationship between wet MD tensile strength and dispersibility. Excluding the KAN01 sample (Figure 4.12), which was

clearly not dispersible because of its longer fibre length, an exponential relationship of the form of Equation 4.1 can be suggested, but clearly, there is only a weak correlation between wet tensile strength and dispersibility.

$$y = -3.58 \times 10^{-7} * \exp(-x/-0.30) + -3.58 \times 10^{-7} * \exp(-x/-0.36) + 100$$

Equation 4.1

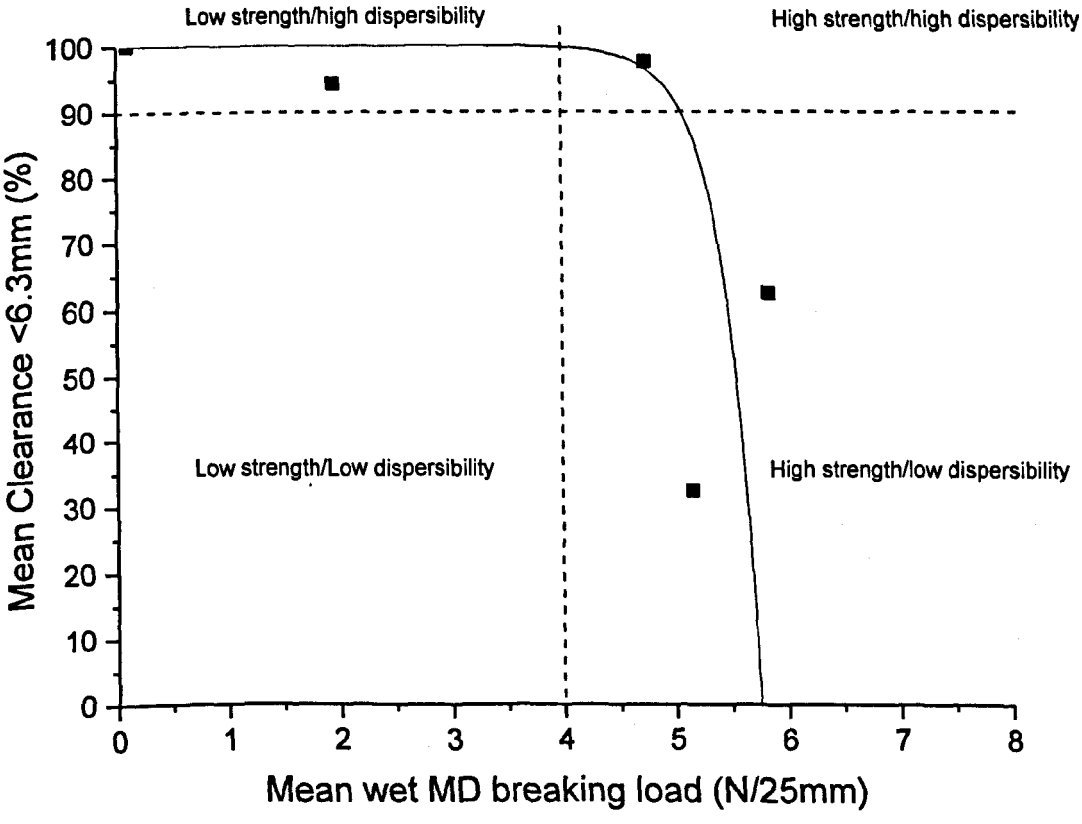


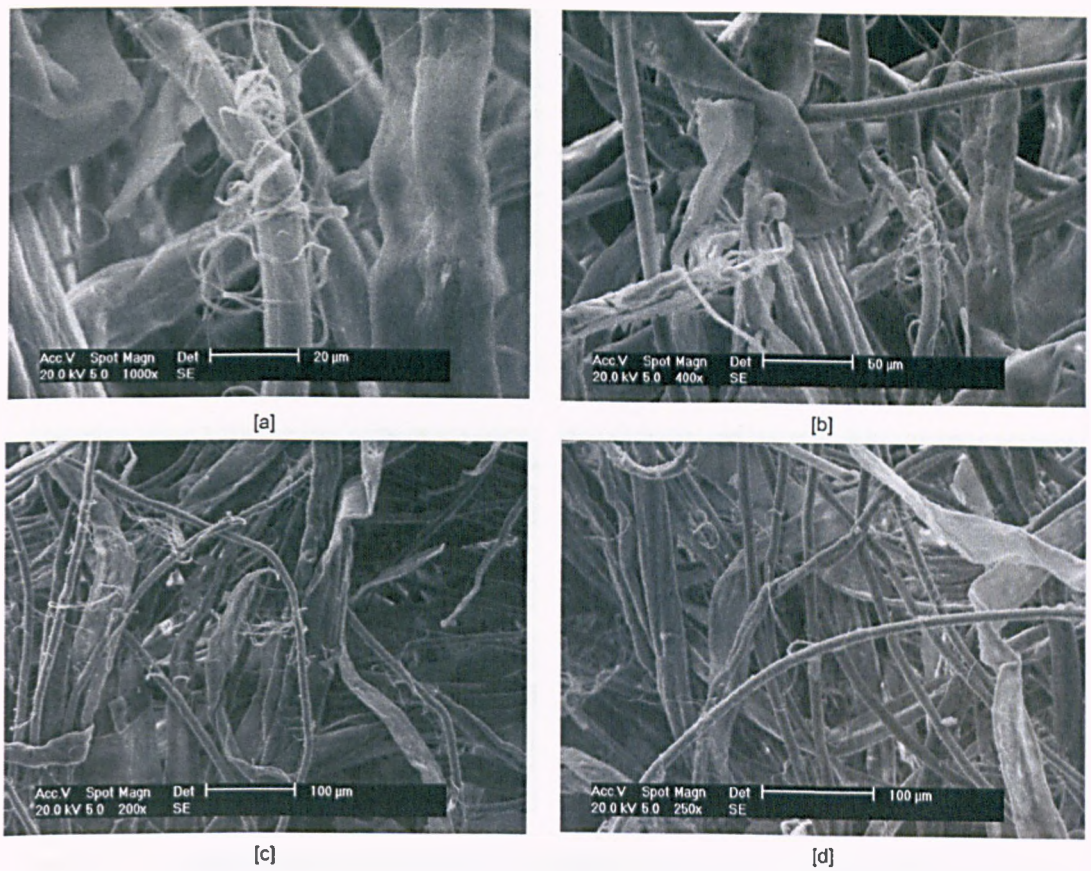
Figure 4.13. Relationship between MD wet tensile strength and mean clearance (<6.3 mm)

The results shown in Figure 4.13 suggest that the relationship between dispersion performance and wet strength is not linear; the commercial wipes exhibit high variation in their properties. Whilst it is reasonable to expect that wipes with low wet tensile strength would exhibit high levels of dispersion, at higher wet strengths there is more variation in the dispersion performance. As

the wet strength increases above 4N, the dispersibility begins to reduce rapidly but not for all of the wipes. Indeed, of the commercial wipes possessing wet strengths above 4.5 N/25mm one disperses almost entirely (96%) whilst two other wipes exhibit much reduced dispersibility (63% and 32%). The data suggests that for mechanically-bonded structures, if wet tensile strength is below a threshold value, dispersibility would be expected to be high. Above the threshold value, the relationship is not linear and other parameters (e.g. bonding, composition, structural architecture) are likely to play an important role in maximising tensile strength and dispersibility.

4.7 SEM of wipe residue after dispersion

Measuring the screen clearance gives an important indication of dispersibility, but it was reasoned that the nature of the fibre agglomerations caught by each screen could also provide useful insights in the mode of break up during the shake flask treatment. Analysis of the fibrous residue caught in the screens after dispersibility testing may also help to identify why fabrics failed to disperse fully and further inform the design of flushable wipe structures. The residual fibres captured in each of the perforated screens were dried and studied by means of SEM (method in section 3.3.4). Figure 4.14 to Figure 4.18 show the microstructure of the loose fibres retained in the screen after a 6 hr dispersibility test, using the methodology detailed in section 3.3.1. Micrographs are presented here from all the screens in which fibre was captured. In some cases the screen caught no fibre and so no observations could be made.



(a) 6.3 mm screen (b) 6.3 mm screen (c) 3.15 mm screen (d) 1.6 mm screen

Figure 4.14. SEM micrographs of wipe substrate AND01 after 6 hr dispersibility testing

The residue of the AND01 wipe captured in each screen appeared to exhibit similar fibre composition and structure, as shown in Figure 4.14. The numerical proportion of wood pulp fibres was reduced compared to the man-made fibre component, which reflects the fact that the shorter pulp fibres were preferentially released from the structure, enabling their passage through the screens. It was evident that fibrillation of the man-made fibre had occurred, an inherent property of lyocell, as a result of the substrates being agitated for an extended period (6 hr) in the shake flask. Interestingly, the fibrillation appeared to have encouraged entanglement with adjacent fibres, which can be expected to hinder dispersion of adjacent fibres.

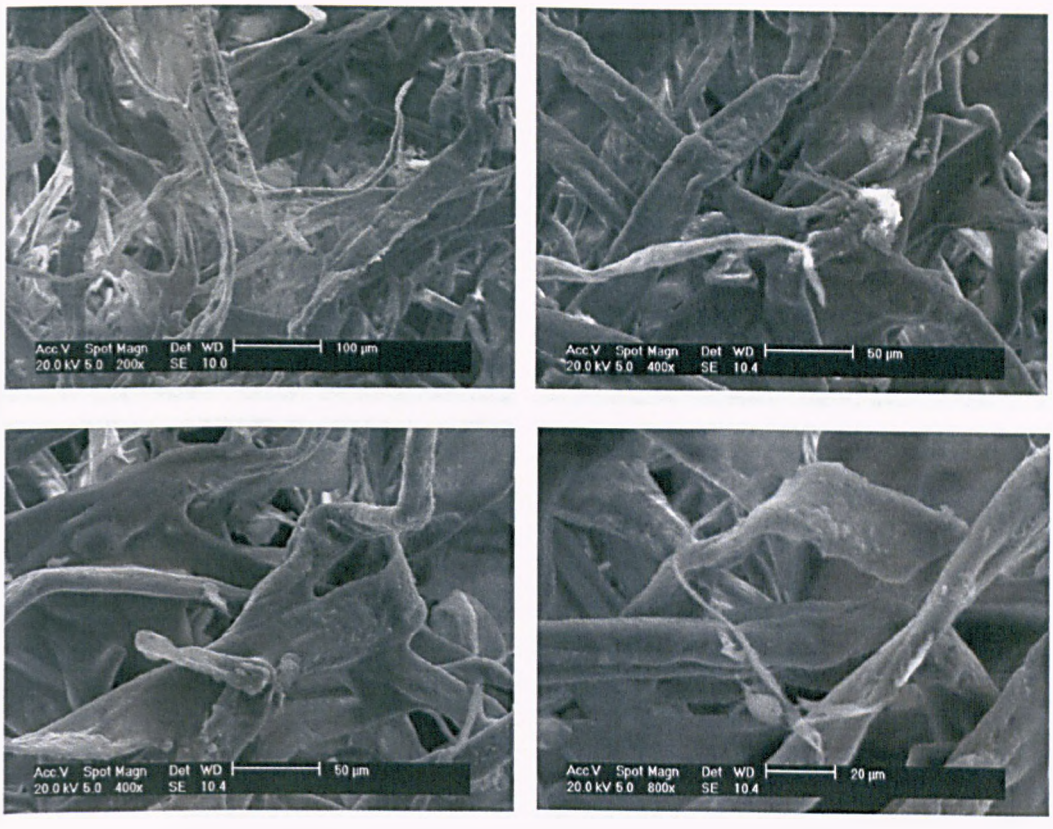


Figure 4.15. SEM micrographs of wipe PAR01 after 6 hr dispersibility testing (12.5 mm screen)

Comparing Figure 4.15 and Figure 4.9, there was no observable difference between the original fabric structure and the structure removed from the screen. The fibres were still covered in chemical binder, which was not removed as a result of dispersibility testing. This is unsurprising given the poor dispersibility of the wipe - the wipe remained almost completely intact.

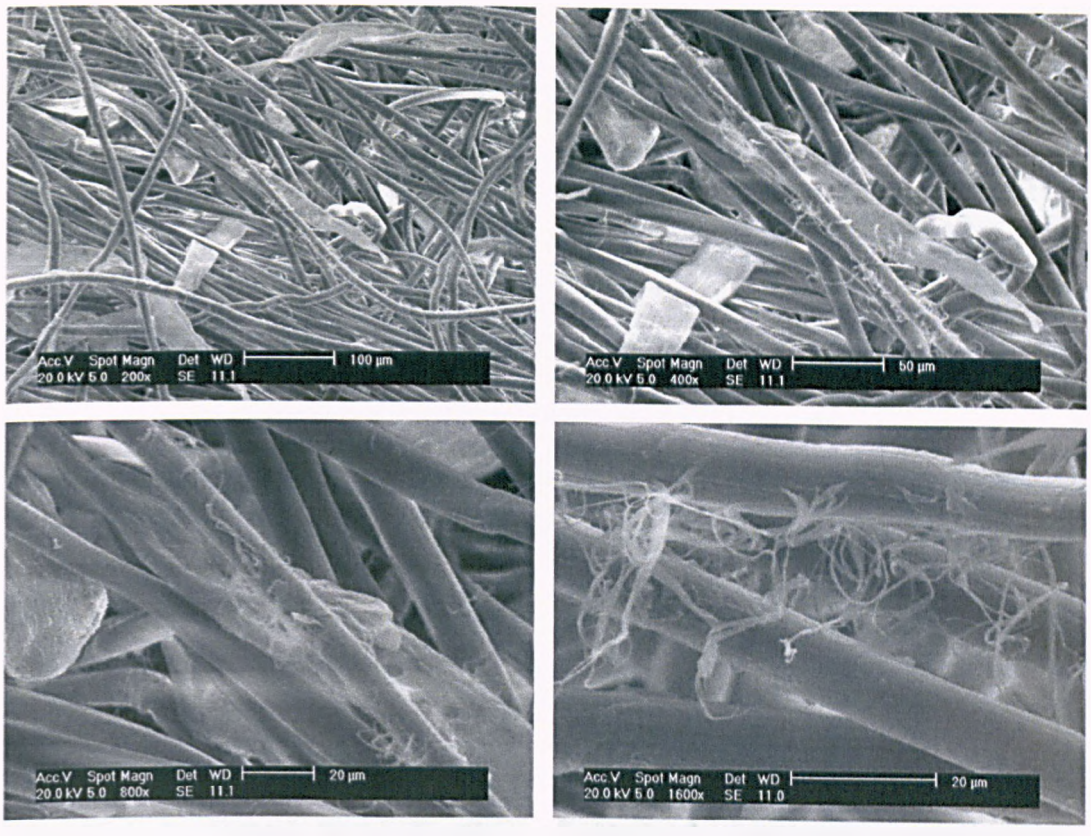
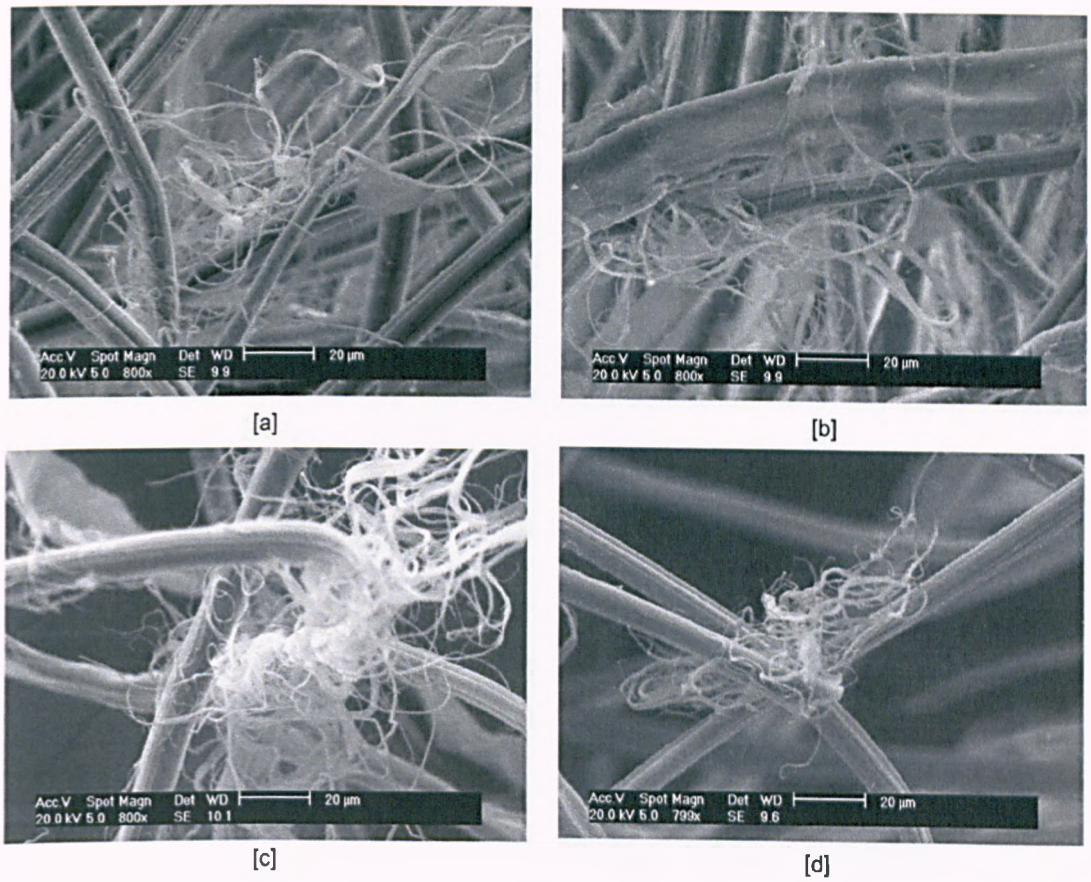


Figure 4.16. SEM micrographs of wipe KAN01 after 6 hr dispersibility testing (12.5 mm screen)

As was observed with the AND01 sample, the KAN01 wipe (Figure 4.16) showed evidence of fibrillation, with entanglements formed across adjacent fibres. Such entanglement might reasonably be expected to impede dispersion and passage through the smaller screens. Again, the majority of fibres retained by the screen comprised lyocell, with relatively few wood pulp fibres suggesting that they preferentially release from the structure during dispersibility testing enabling passage through the screen.

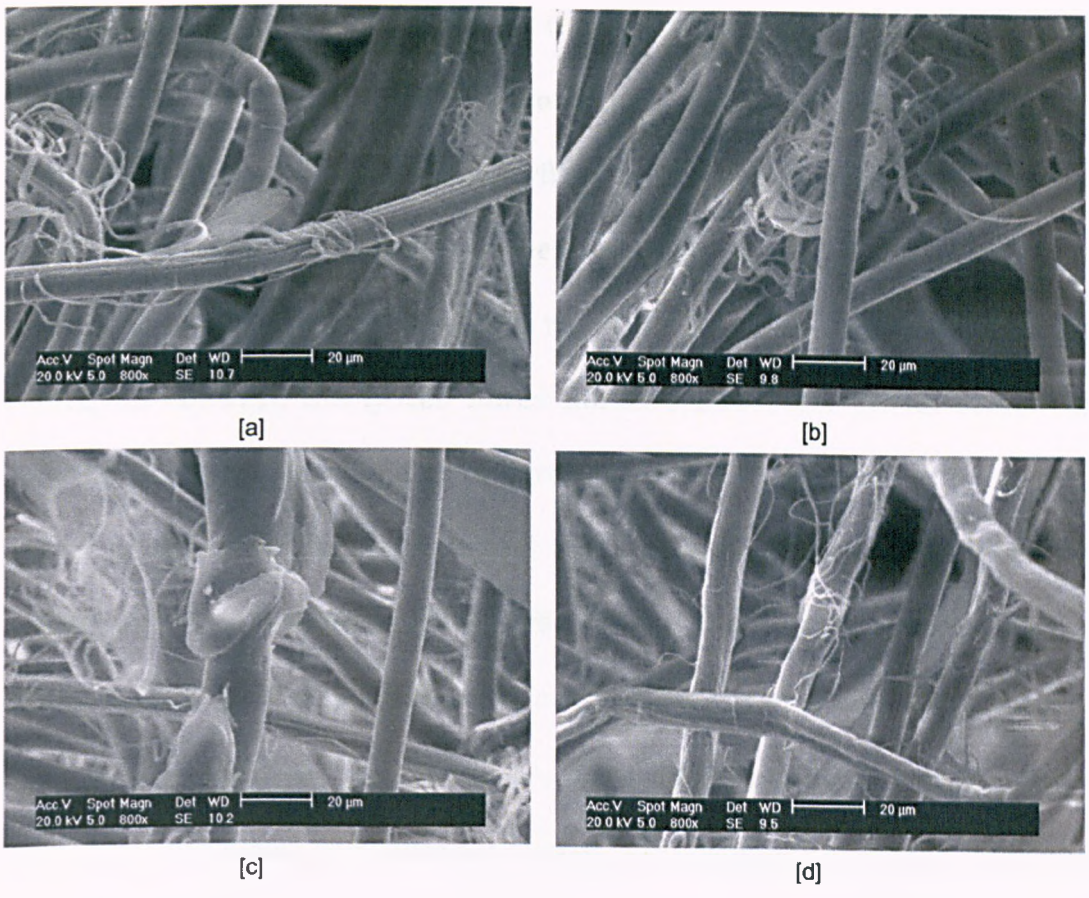


(a) 6.3 mm Screen (b) 6.3 mm Screen (c) 3.15 mm Screen (d) 1.6 mm Screen

Figure 4.17. SEM micrographs of wipe UNI01 after 6 hr dispersibility testing

The residual fibres from wipe UNI01 caught in the 1.6-6.3 mm screens are shown in Figure 4.17. Again, fibrillation was observed in these entangled entities, with relatively few pulp fibres. This fibrillation is surprising given that the regenerated cellulose fibres are viscose-like in appearance (striated). It is possible that the wipe comprises polynosic viscose (high wet strength), which is more susceptible to fibrillation than viscose in a similar manner to lyocell (119).

The structure of the residual fibre material obtained for wipe CAR01 is shown in Figure 4.18 and the trend was repeated.



(a) 12.5 mm Screen (b) 6.3mm Screen (c) 3.15mm Screen (d) 1.6mm Screen

Figure 4.18. SEM micrographs of wipe CAR01 after 6 hr dispersibility testing

In a few locations within the CAR01 sample, characteristic morphology was observed consistent with thermal bonding. For example, the fibre shown in Figure 4.18(c) is suggestive of interfacial thermal bond breakage. Although, not detected by FTIR, the patent which underpins sample CAR01 (120) indicates that a small proportion (1-2%) of thermoplastic core-sheath binder fibre is introduced to facilitate thermal bonding after hydroentanglement to improve wet strength (120).

The SEM results for the commercial wipe samples after dispersibility testing (Figure 4.14 to Figure 4.18), revealed fibrillation of the lyocell fibres in all the wipes except PAR01. Lyocell has been widely reported to fibrillate in wet

abrasion conditions (117, 143, 245) so it noteworthy, if not surprising, that the mechanical agitation in aqueous conditions, which takes place in the dispersibility test, results in fibre fibrillation. In samples KAN01, CAR01 and UNI01 high levels of lyocell can be observed compared to wood pulp, suggesting a large proportion of the wood pulp has been dispersed during testing. In contrast, the lyocell fibres fibrillate and these fibrils appear to increase the mechanical bonding of fibres, which can be expected to reduce the ability of the fibres to separate and disperse during dispersibility testing. AND01 exhibited a reduced level of fibrillation, which could account for the comparatively good dispersion performance that was observed (Figure 4.14). Wipe PAR01 exhibited no fibrillation, as it did not contain lyocell. Some splitting of the wood pulp fibre was noted but essentially the wipe remained intact, held together by the binder.

4.8 Summary

Given the extent of the patent literature detailed in section 2.5 to 2.7, few flushable wet wipe technologies have so far been widely adopted. This in part reflects the difficulties of balancing the conflicting needs of high wet strength and rapid dispersibility such that residual material is sufficiently small to clear the screens. Of the current state-of-the-art flushable wipes, all were found to consist primarily of cellulose and the majority were found to comprise blends of wood pulp with at least one other short-cut man-made fibre component, consisting typically of regenerated cellulose. KAN01 exhibited the highest wet tensile strength but was not dispersible and therefore cannot be considered

flushable. The wipe exhibiting the best balance of wet strength and dispersibility (AND01) was constructed using airlaying and chemical bonding. This triggerable binder technology is however heavily patented by Kimberly Clark and known to be quite expensive. Of the other best performing wipes (CAR01, UNI01), bonding was achieved by hydroentangling. The degree to which the apparently conflicting requirements of high wet strength and dispersibility can be improved by adjusting fibre dimensions, relative fibre compositions and hydroentangling machine settings is not yet known. These parameters will be investigated in Chapter 5. It is clear that none of the commercial wipes meet the aspiration specification set out in 2.9.

Chapter 5

The influence of fibre composition and hydroentangling conditions on fabric tensile properties and dispersibility

Given the current industry flushability guidelines and available materials, it is apparent that the specific combination of requirements that govern the viability of a wet wipe substrate in terms of cost, liquid absorption and ability to biodegrade in aerobic conditions, are most readily satisfied by a short fibre, cellulose-based composition. This is further reinforced by the commercial substrates studied in Chapter 4 all of which were found to mainly comprise of cellulose in wood pulp or regenerated cellulose forms of short fibre length. It was also established that the frictional bonds generated by hydroentangling are also reversible to extent during flushability testing, enabling release of constituent fibres creating a dispersible fibrous network. However, the degree to which a balance of high wet strength and dispersibility can be more effectively balanced in such fabrics is not yet known, and there may be opportunities to improve fabric properties and dispersibility by adjusting fibre dimensions, relative fibre composition and fibre entanglement during fabric manufacture. The key factors to be considered were summarised in Table 2.2. Accordingly, in this chapter, a systematic study of the effects of fibre length, diameter, fabric composition and hydroentangling process settings was conducted to establish the influence on fabric wet strength and dispersibility.

5.1 Experimental Plan

The cellulosic fibre-related parameters considered important were dimensions (length and fineness), fibre tensile properties and surface friction. The density of cellulosic fibres does not vary considerably and it is impractical to produce non-circular (e.g. trilobal) cross-sections at low linear densities (below 3.3 dtex), resulting in poor bonding conditions during hydroentanglement. The fibre specifications and methods of manufacture are detailed in Table 3.1 and Section 3.2.1 to 3.2.4. To enable comparison of the experimental fabrics, the web area density was in the narrow range of 60-70 $g.m^{-2}$, which approximates currently available commercial flushable wipe substrates. Fabrics were produced by wetlaying and airlaying to enable a comparison of the properties produced by each. The effect of fibre blend proportion was investigated, increasing regenerated cellulose fibre content whilst decreasing wood pulp. The fibre orientations are largely defined by the airlaid and wetlaid processes in combination with the bonding conditions; controlled variation is not possible. The degree of bonding developed in the web during hydroentangling is dependent on the specific energy consumed during manufacture, which can be modulated by changing the water pressure as well as other parameters as indicated in Table 2.5. The angle of jet impingement was kept constant at 90° to reflect common commercial practice, although changes in angle have a limited influence on properties (252). Since the conveyor structure is also known to influence bonding (152, 253), the influence of its open area on wet tensile properties was also studied. Note that in the experiments that follow, the wet breaking load and dispersibility data refers to fabrics that are impregnated

with a commercially utilised wet wipe lotion (section 3.2.4), to properly simulate real conditions. Details of the lotion and the methods of preparing samples are detailed in section 3.1 and 3.2.

5.2 Fibre-related factors

The influence of fibre dimensions, specifically mean fibre length and fineness on wet strength and dispersibility was investigated since these dimensions will affect the frictional resistance of the fibre network. The fibre fineness will influence the total number of fibres and specific surface area within the wipe structure as well as the fibre bending mechanics and propensity to form fibre entanglements. Fibre length is particularly influential on fibre entanglement, as detailed in section 2.6.6. This is particularly important in nonwovens containing short fibres where very small increases in fibre length can be expected to create more inter-fibre frictional contacts and for entanglements to involve a greater number of surrounding fibres.

5.2.1 Influence of fibre length in wetlaid hydroentangled fabrics

The way in which fibre length affects the wet tensile strength of wetlaid fabrics is shown in Figure 5.1. The fabrics comprised of 80:20 wood pulp:lyocell blends hydroentangled with 0.769 $MJ.kg^{-1}$ specific energy. The linear density of the lyocell 1.4 dtex and the fibre length was systematically varied from 6, 8 and 10 mm.

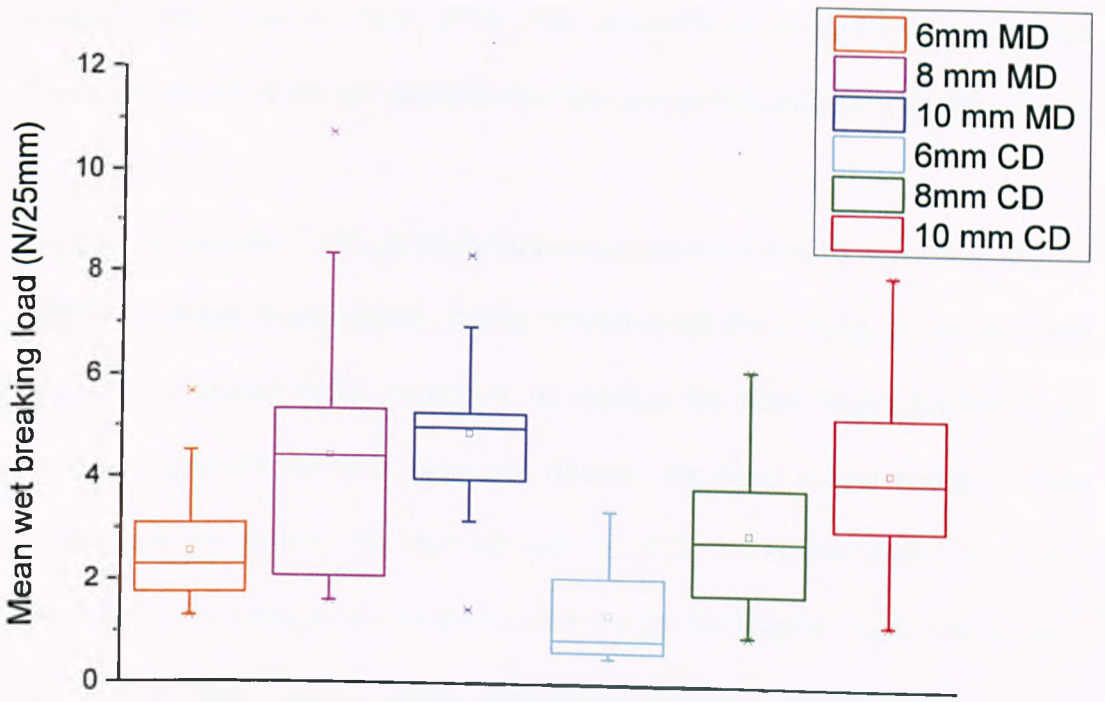


Figure 5.1. Influence of fibre length on MD and CD wet tensile strength of wetlaid-hydroentangled wood pulp-lyocell (1.4 dtex) fabrics

As fibre length increased the wet tensile strength of the wetlaid fabric increased, reflecting higher frictional resistance to fibre slippage. Thus, over the fibre length range studied, a positive relationship was found between fibre length and wet tensile strength. A one-way ANOVA confirmed a statistically significantly difference between the means at the 0.05% level ($F = 9.68866$, $p = <0.001$). The variation in wet tensile strength may reflect short-term weight variations or small differences in the spatial arrangement of lyocell fibres between test specimens.

The basic trend between tensile strength and fibre length is consistent with previously reported results in which the strength of wetlaid-hydroentangled fabrics composed purely of regenerated cellulose increased as fibre length

changed from 4mm to 8mm (75). The strength of carded-hydroentangled fabrics respond in a similar manner, as reported by Bartholomew (122).

However, as revealed in Figure 5.2, increasing the fibre length in wetlaid fabrics negatively affects dispersibility. Whilst fabrics made from either 6 mm or 8 mm fibres still exhibited >95% clearance, increasing the fibre length further to 10 mm, led to greatly reduced clearance despite the fibre length being 2.5 mm smaller than the screen hole size (10 mm vs. 12.5 mm respectively). Note that in Figure 5.2 the clearance data presented are for the largest (12.5 mm) screen, which could retain much smaller amounts of fibre compared to the smaller screen sizes.

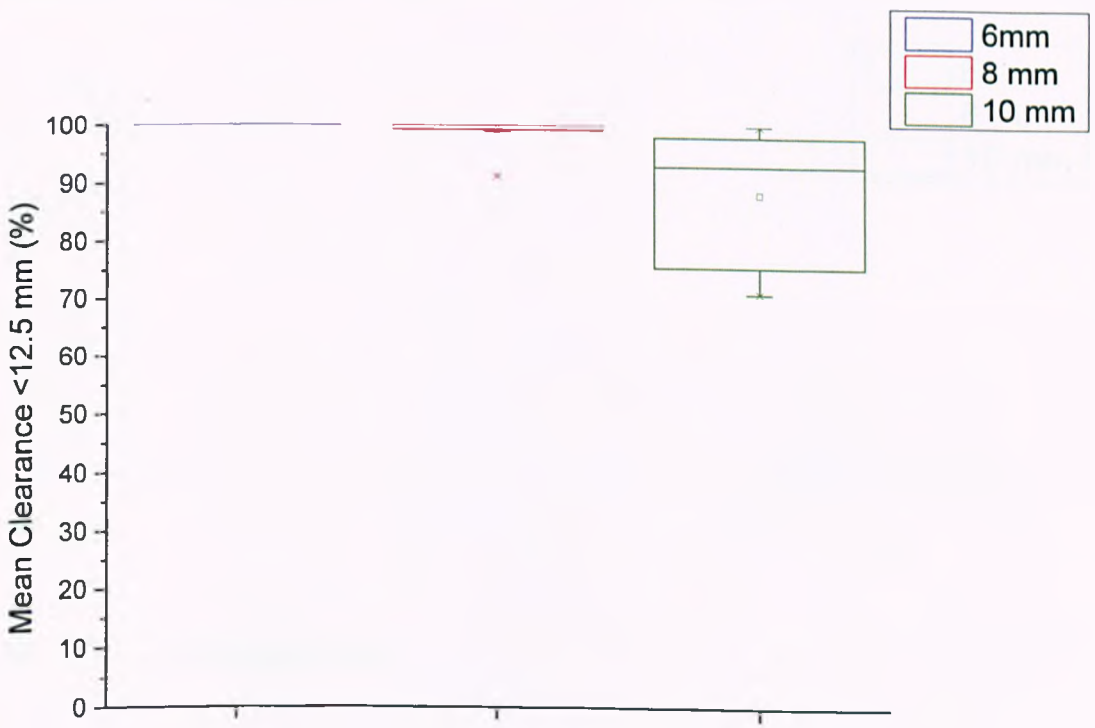


Figure 5.2. Influence of fibre length on dispersibility of wetlaid-hydroentangled wood pulp-lyocell (1.4 dtex) fabrics

The fact that clearance is not simply dependent on the ratio of fibre length to the prevailing screen size, may suggest that fibres in the fabric are not

completely released or disintegrated into an individualised form during their time in the shake flask. Incomplete disintegration or agglomeration of fibres following disintegration would lead to relatively large collections of fibres that are less likely to clear the screen holes.

5.2.2 Influence of fibre length in airlaid hydroentangled fabrics

The experiment was repeated for airlaid webs using the same 80:20 wood pulp:lyocell blends hydroentangled with 0.769 $MJ.kg^{-1}$ specific energy. The linear density of the lyocell 1.4 dtex and the fibre length was systematically varied from 6, 8 and 10 mm. A similar positive relationship between wet MD tensile strength and fibre length was observed in airlaid-hydroentangled fabrics, as shown in Figure 5.3.

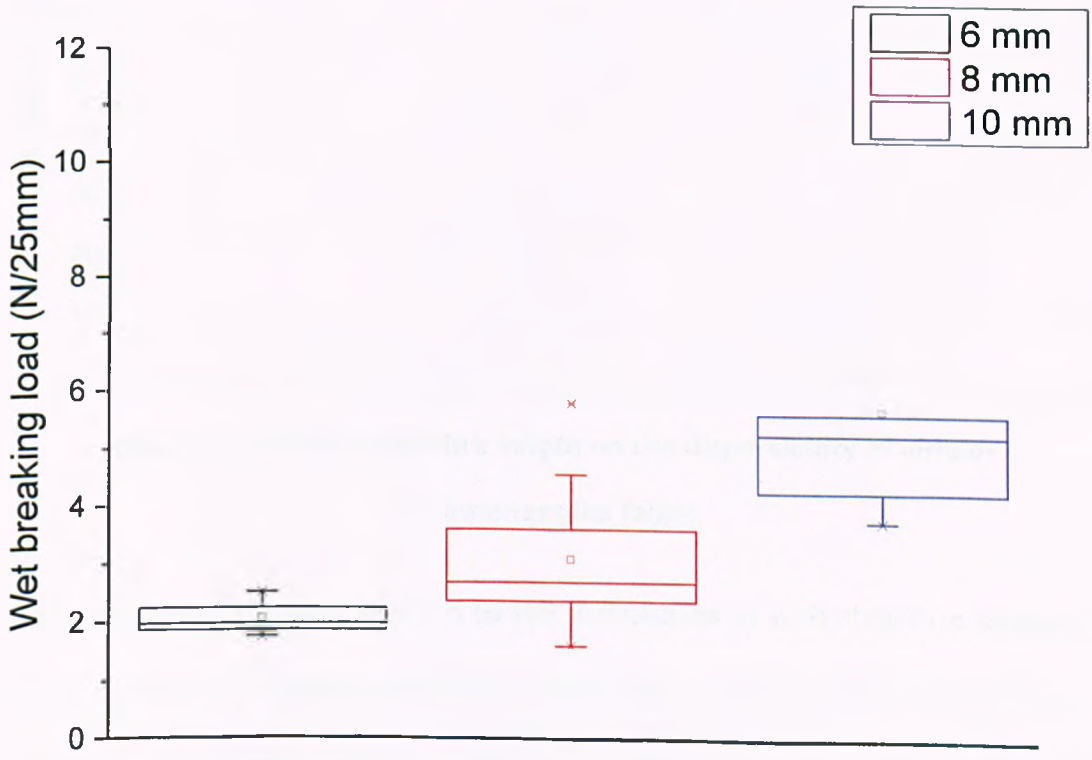


Figure 5.3. Influence of fibre length on MD wet tensile strength of airlaid-hydroentangled wood pulp-lyocell (1.4 dtex) fabrics

Significant differences were obtained between the means at the 0.05% level ($F = 10.81$, $p = <0.001$). In contrast to the wetlaid fabrics (Figure 5.1), the airlaid fabrics exhibited a narrower variance of wet tensile strength data for a given fibre length. Figure 5.4 shows the relationship between fibre length and dispersibility for airlaid fabrics. As with the wetlaid samples, dispersibility decreased with increasing fibre length, although the clearance was more sensitive to changes in fibre length in the airlaid structures.

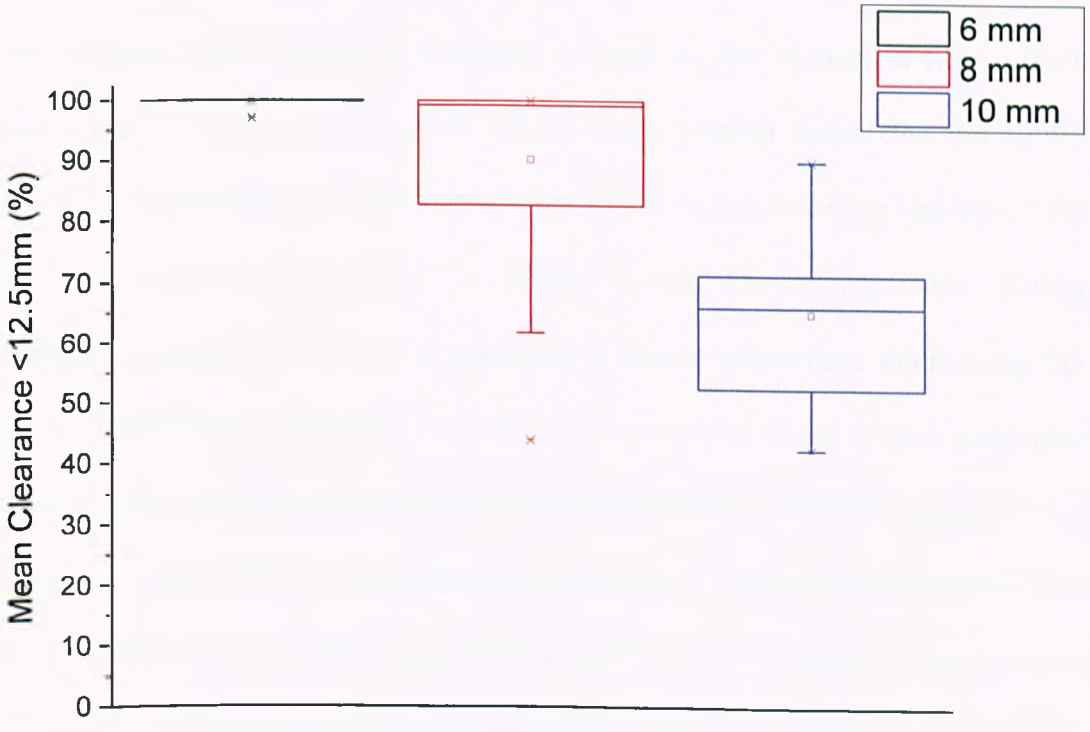


Figure 5.4. Influence of fibre length on the dispersibility of airlaid-hydroentangled fabric

This difference can be attributed to the differences in web structure achieved using airlaid and wetlaid processes. Wetlaying creates denser webs due to hydrodynamic forces applied to the web during laydown which is likely to restrict fibre movement during hydroentanglement, reducing the ability of the fibre to be reorientated by the water jet. Airlaying creates more open webs, which enables the greater levels of fibre movement by the water jet of the same

energy. Denser webs could also be expected to result in less effective water removal during hydroentanglement reducing energy transfer by the water jets as well as limiting energy transfer back from the conveyor belt (75). For the same fibre composition entanglement is likely to be higher in hydroentangled materials produced by airlaying compared to wetlaying.

5.2.3 Fibre aspect ratio

The fibre linear density is important because of its effect on both the aspect ratio (length divided by the diameter) as well as the numerical fibre blend. Additionally, fibre dimensions will influence mechanical properties and ability to form entanglements. Fine fibres tend to lead to low bending rigidity (124) and consequently may lead to higher levels of entanglement during hydroentangling. For the same gravimetric blend proportion, decreasing the linear density will increase the numerical frequency of fibres of that particular component. Increasing the aspect ratio is also helpful in minimising roping and a value of 400-3000 is reported to be a preferred range (136). Based on the data obtained for the fabrics reported herein, the relationship between aspect ratio and MD wet tensile strength for airlaid and wetlaid fabrics is shown in Figure 5.5. Airlaid and wetlaid 80:20 wood pulp:lyocell fabrics were hydroentangled at 0.769 $MJ.kg^{-1}$, the wood pulp types used in each process are detailed in 3.1. The wetlaid materials were composed of 1.4 dtex and 1.7 dtex fibres at 6, 8 and 10 mm fibre lengths for both linear densities. The wood pulp airlaid material comprised 20% by weight 1.7 dtex (6, 8 mm) and 1.4 dtex (8, 10) lyocell fibres. By varying the fibre length a greater range of aspect ratios

was studied as lyocell fibres are only available in a limited range of linear densities.

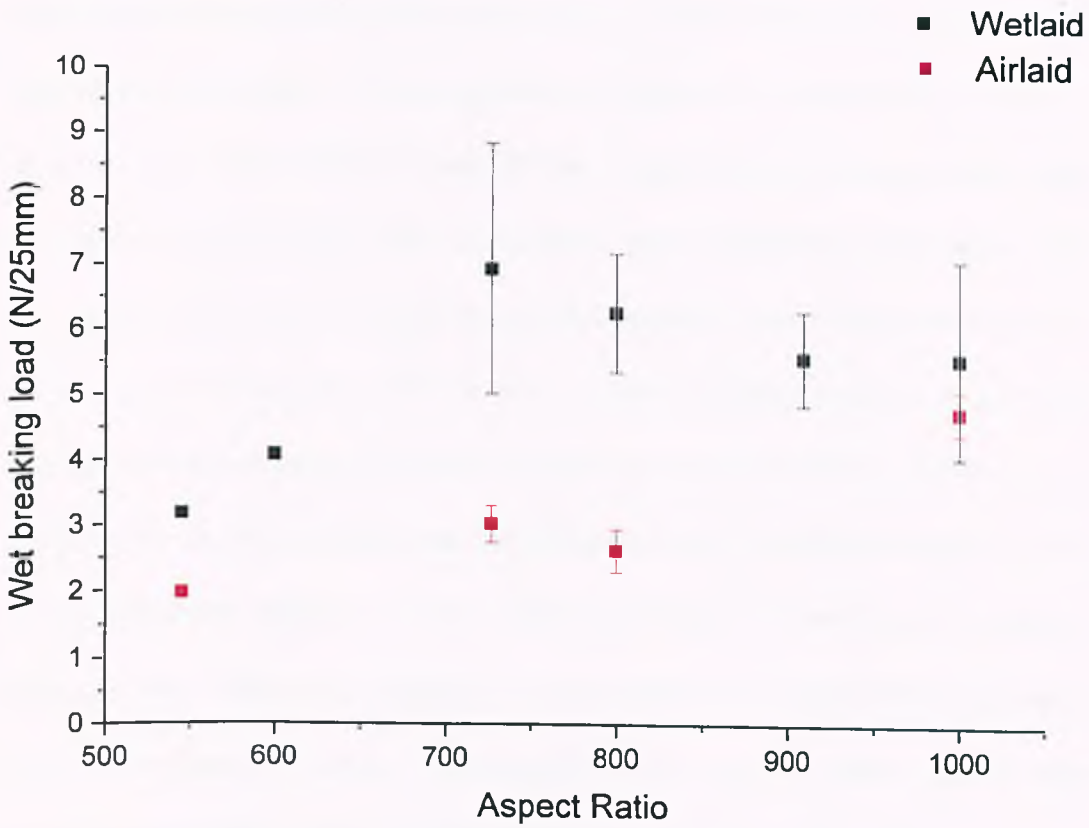


Figure 5.5. Influence of aspect ratio on MD wet tensile strength of airlaid-hydroentangled and wetlaid-hydroentangled wood pulp-lyocell fabrics

Surprisingly, the trends in the data for the airlaid and wetlaid fabrics are rather different. For the airlaid-hydroentangled fabrics, wet tensile strength values increased steadily as the aspect ratio increased up to 1000, whereas the wetlaid fabric values peaked at about 700, and leveled thereafter. Woodings (76) also reported that carded-hydroentangled fabric strength increased with increasing aspect ratio but that the relationship with wetlaid materials was found to be more complex. Inherent differences in the original web densities of wetlaid and airlaid substrates prior to hydroentangling could help to explain the observed differences. Wetlaying creates a dense fibre web due to the hydrodynamic

forces involved in collecting fibres on the conveyor. This reduces the mobility of fibres during subsequent hydroentangling because the fibre web is already substantially compacted, limiting the ability of fibre ends to be migrated and twisted in to the form of entanglements. Airlaying, in contrast, produces a lower density initial web, in which the normal forces acting at the fibre intersections will be lower than in wetlaid webs, facilitating their movement and entanglement more readily during the bonding step. A high web density could also result in less effective water removal during hydroentanglement leading to reduced energy transfer by the water jets. Given that the fibres in airlaid webs can be entangled more intensively than is possible in wetlaid webs, the optimal fibre length for airlaid wipes is perhaps shorter than for wetlaid since the fibres will be more difficult to disentangle in the shake flask leading to greater resistance to fabric disintegration. The way in which aspect ratio influenced the dispersibility of wetlaid fabrics is shown in Figure 5.6.

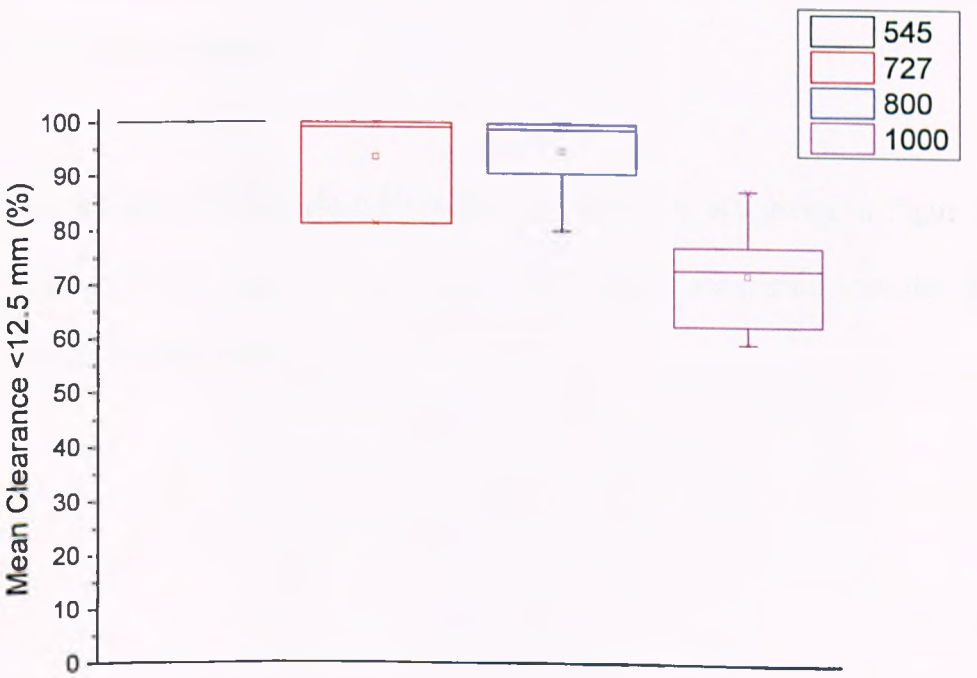


Figure 5.6. Increasing aspect ratio reduces dispersibility in wetlaid-hydroentangled wood pulp-lyocell wipes

As the aspect ratio increased there was greater variation in dispersibility and mean clearance was negatively affected above an aspect ratio of 800. This suggests that for practical purposes, the upper limit for aspect ratio is much lower than the value of 3000 previously suggested by Tanio et al (136).

5.2.4 Structural differences in the airlaid-hydroentangled and wetlaid-hydroentangled fabrics determined by x-ray microtomography

Given the basic differences between airlaid and wetlaid web architectures and packing density prior to hydroentangling it was instructive to determine if any distinguishing structural features could be identified that could help to explain the observed differences in dispersibility. Using, X-ray microtomography 3D images of each fabric was obtained without recourse to disruptive cross-sectioning techniques (methodology is given in section 3.3.6). In each of the following images, the fabrics are of the same composition (80:20 pulp:lyocell, 1.4 dtex, 6 mm) and the fabrics were hydroentangled using identical specific energies (0.72 $MJ.kg^{-1}$).

Tomographs of the airlaid-hydroentanged fabrics are given in Figure 5.7 and Figure 5.8 and the corresponding wetlaid-hydroentangled samples in Figure 5.9 and Figure 5.10.

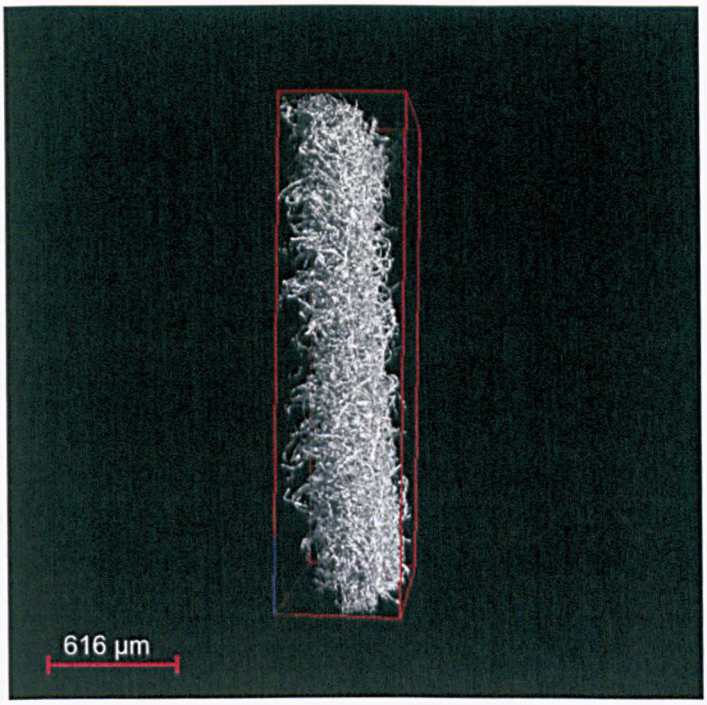


Figure 5.7. Tomograph of 80:20 wood pulp-lyocell (6mm, 1.4 dtex) airlaid-hydroentangled fabric - Cross-section showing migration of fibre segments through-plane

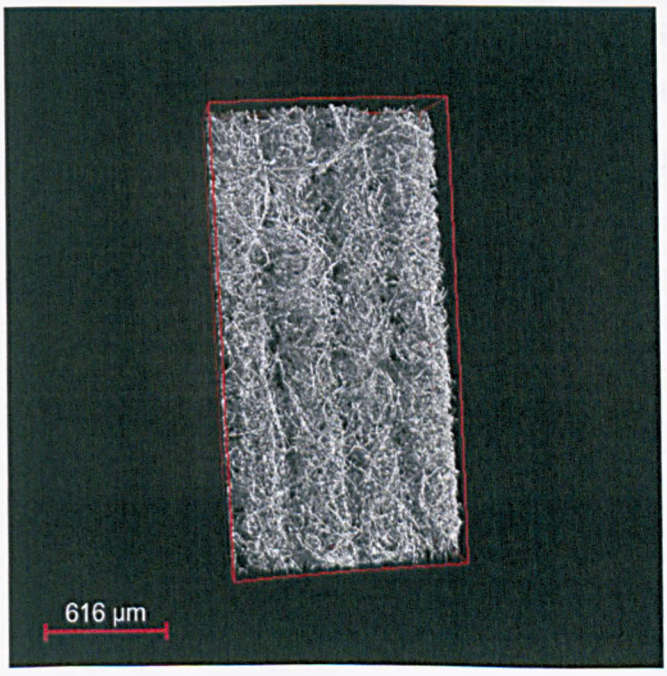


Figure 5.8 Tomograph of 80:20 wood pulp-lyocell (6mm, 1.4 dtex) airlaid-hydroentangled fabric - Upper face showing jet marks from hydroentangled in the machine direction (north-south)

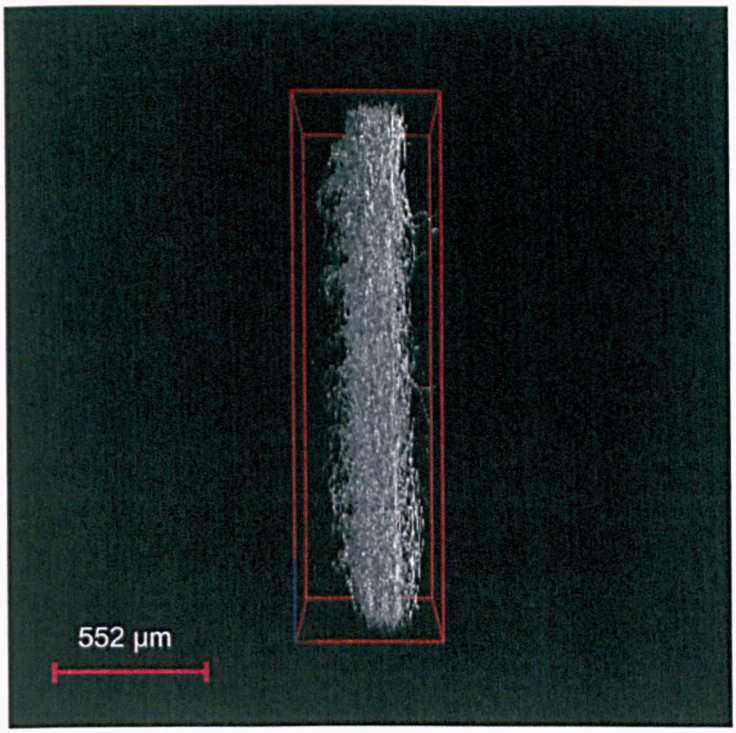


Figure 5.9 Tomograph of wood pulp-lyocell (1.4 dtex, 6 mm) wetlaid-hydroentangled fabric - Cross-section, showing planar orientation of fibres

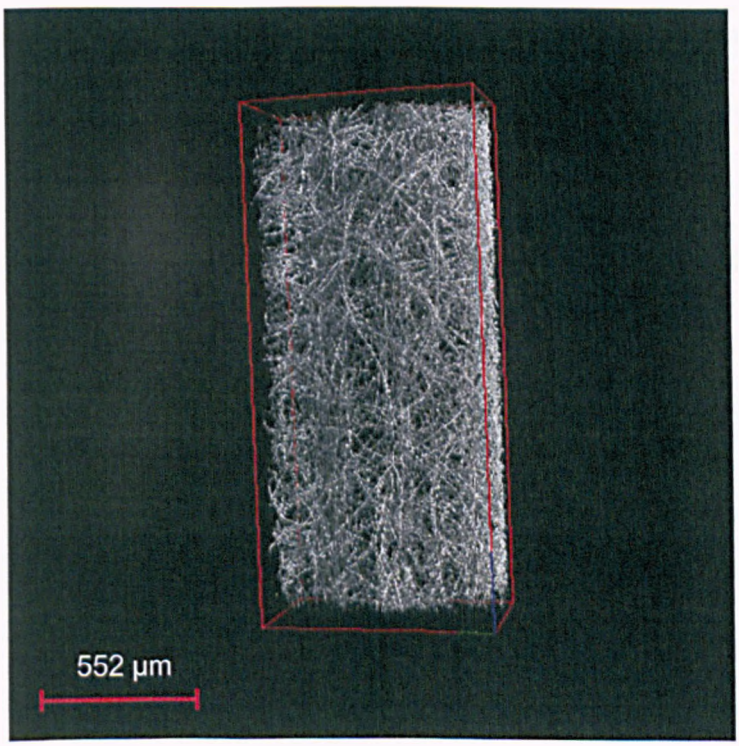


Figure 5.10 Tomograph of wood pulp-lyocell (1.4 dtex, 6 mm) wetlaid-hydroentangled fabric - Upper face showing limited out-of-plane migration of fibre segments

Nonwoven structures can be considered in terms of fibres arranged in at least dimensional planes, X, Y and Z (Figure 5.11).

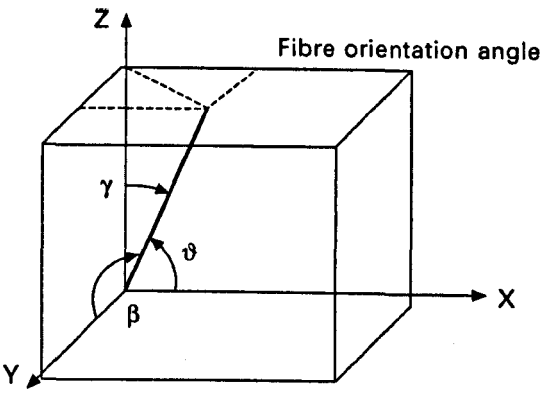


Figure 5.11 Fibre orientation angle in three-dimensional nonwoven fabrics, adapted from Russell (254)

In practice, the majority fibres are arranged in the X and Y planes (MD and CD) (254). Although fibre alignment in both the airlaid and wetlaid fabrics is mostly in the X and Y planes, it is apparent in Figure 5.7 and Figure 5.8 that a degree of through-plane fibre segment migration in the airlaid fabrics occurs, whereas it is absent in the wetlaid samples. The wetlaid fabric remains highly planar and it results in a thinner, more compact structure compared to the airlaid fabric with fewer fibres protruding from the underside of the fabric. Local fibre displacement, due to interaction between the water jets and fibres during hydroentanglement can clearly be observed on the upper surface of the airlaid structure. Similar disturbance and displacement of fibres in the wetlaid fabric is barely discernible.

The packing density of the web presented to the jets during hydroentangling and the ability of fibres to be displaced, are likely to have a major influence on

the final fabric properties. Wetlaid webs tend to be denser due to hydraulic forces acting upon the fibres through the forming wire at the point of laydown. Fibres also tend to be deposited in a flat, planar orientation. Airlaid webs are more voluminous and the web is thicker than a wetlaid of similar basis weight during deposition. These differences in web structure are likely to influence the extent to which fibre segments are frictionally restricted from displacing during hydroentangling and therefore the degree to which fibre entanglement and strength can be developed in the fabric.

5.3 Influence of cellulosic fibre composition on fabric strength and dispersibility

In addition to fibre dimensions, the fibre composition of a fabric can be expected to have a strong influence on fabric properties because of for example, inherent differences in mechanical properties and hygroscopic behaviour. Commercially, the two most important regenerated cellulose fibres associated with wet wipe manufacture are viscose and lyocell, but there have been no academic studies that consider their relative wet strength and dispersibility properties in relation to airlaid-hydroentangled and wetlaid-hydroentangled fabrics. Accordingly, a study was made of the wet strength and dispersibility of fabrics containing both fibres, in blends with wood pulp. The effect of changing the proportion of wood pulp in blends with these regenerated cellulose fibres, was also conducted, to determine the degree to which the blend could be diluted with a lower cost cellulose component (wood pulp).

5.3.1 Comparison of the tensile strength and dispersibility of wetlaid-hydroentangled fabrics containing viscose and lyocell

Wetlaid-hydroentangled wipes composed of 80:20 wood pulp:lyocell of 8 mm fibre length and 1.7 dtex lyocell or viscose of the same dimensions, were hydroentangled with a specific energy of 0.769 $MJ.kg^{-1}$. The results are shown in Figure 5.12.

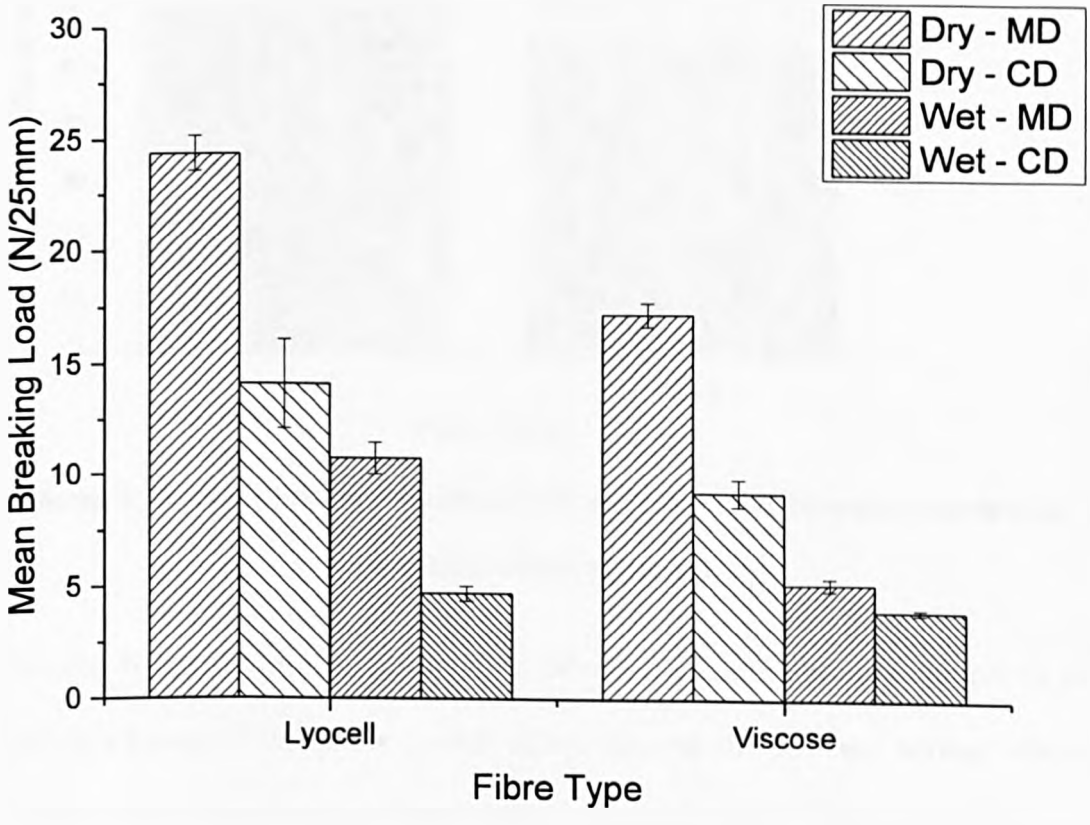


Figure 5.12. Wet and dry tensile strength of wetlaid-hydroentangled fabrics composed of 80:20 wood pulp:lyocell and 80:20 wood pulp:viscose produced using identical hydroentangling conditions

As reported by Bertram in relation to carded-hydroentangled fabrics (75), substituting lyocell for viscose resulted in increases in both dry and wet tensile strength in the MD and CD. The dry MD strength increased substantially by 42% from 17.2 to 24.4 N/25mm. As expected, the wet tensile strengths were

consistently lower compared to the dry for both the lyocell and viscose-containing fabrics. The dispersibility of the two fabrics is shown in Figure 5.13.

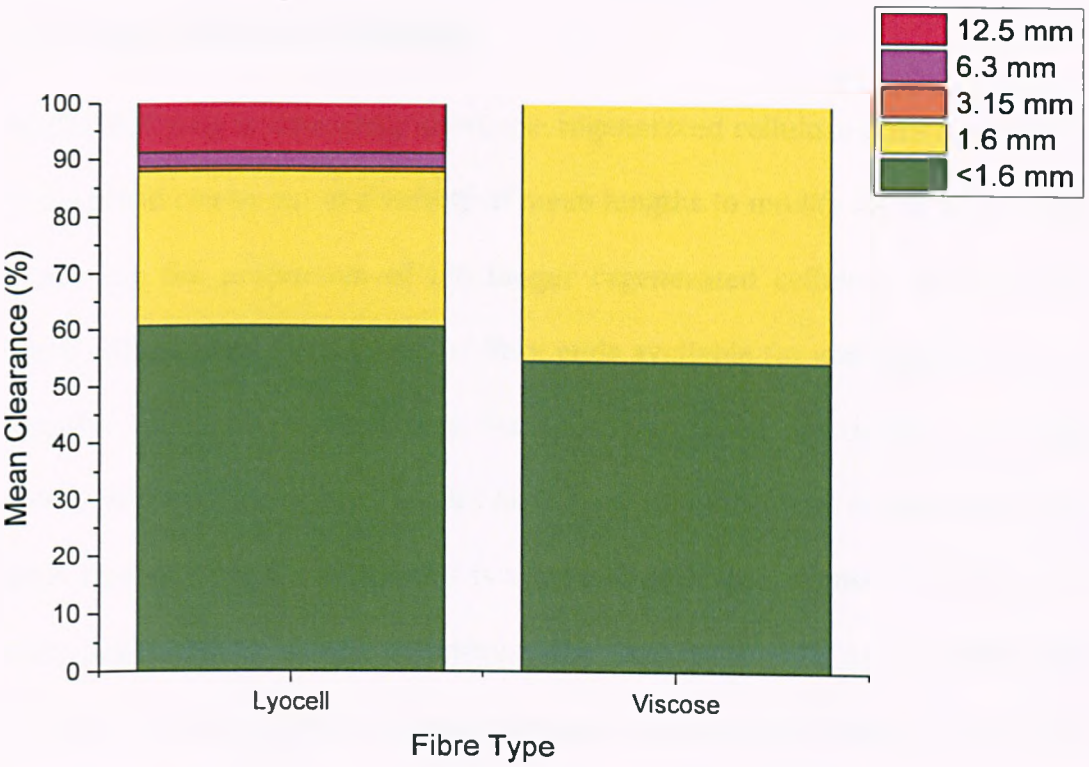


Figure 5.13. Dispersibility of wetlaid-hydroentangled 80:20 wood pulp:lyocell and 80:20 viscose fabrics

Greater dispersibility was observed in fabrics containing viscose compared to lyocell wherein 88% of the lyocell fabric cleared the 6.3 mm screen whilst 100% of the viscose fabric cleared the same screen. The reasons for this are intriguing. The low wet modulus of the viscose fibres, compared to lyocell, would be expected to give rise to substantial fibre entanglement during hydroentangling, mitigating rapid disintegration of the fabric in the shake flask. However, the degree of entanglement is likely to have been limited by the low specific energy employed during manufacture of the samples (0.769 $MJ.kg^{-1}$). It is possible that the low wet modulus of the viscose is influential in assisting disintegration of the fabric when it is saturated in water and agitated in the

shake flask, allowing fibres to disentwine and slide over each other, undermining the frictional resistance to slippage.

5.3.2 Effect of blend proportions

Whilst fluff pulp is inherently short, the regenerated cellulose fibre component in the blend can be cut to a variety of mean lengths to modify fabric properties. Increasing the proportion of the longer regenerated cellulose fibres in the blend will increase the number of fibre ends available for entanglement, but a negative effect on dispersibility would obviously be anticipated. Although 100% pulp hydroentangled fabrics have been manufactured in the past (230), their strength, both wet and dry is very low such that chemical bonding has been suggested as means to address the limitation. (77) As an alternative strategy, blends of wood pulp and longer regenerated cellulose fibres have been successfully employed, although the longer fibre component comprises a maximum of 25-30% by weight to ensure uniform web formation during wetlaying or airlaying as well as acceptable economics. Viazmensky (59) studied the properties of hydroentangled fabrics containing wood pulp and 5-30% short cut fibre and below 20% fabrics were very weak without the addition of a binder. Lang (69) studied fabrics composed of 75% lyocell, 25% wood pulp and found that they did not disperse effectively. Commercially, there is an incentive to incorporate as much wood pulp as possible because it is substantially cheaper than short cut man-made fibre. However, despite the economic advantage, high wood pulp content compromises fabric softness as well as the wet strength of the final product. Thus, there is a threshold blend proportion of about 20% by weight of short cut cellulose fibre below which,

wood pulp-rich, binder-free fabrics with sufficient wet strength cannot be manufactured. Above 30% by weight, cost-effective manufacture as a wet wipe substrate becomes prohibitive. A blend proportion of 20-30% for the regenerated cellulose fibre is therefore the most relevant window for further development and this is reflected in the present study.

The relationship between wet and dry breaking load and the proportion of lyocell in the blend was explored, together with dispersibility. These experiments were conducted using Tencel A100 with a mean fibre length 10 mm and a linear density of 1.4 dtex in blends with wood pulp of 20%, 25% and 30% by weight. The fabrics were wetlaid and hydroentangled with a specific energy of 0.769 $MJ.kg^{-1}$. As indicated in Figure 5.14 the wet and dry MD tensile strength both increased as the proportion of short-cut fibre increases in the blend.

In the dry state the increases in MD tensile strength were not necessarily proportional to the lyocell content, probably due to the influence of hydrogen bonding, which is likely to contribute to dry strength. It is also possible that a threshold content (e.g. above 25%) of lyocell is required to have a substantial impact on improving tensile strength. Similar results were observed by Lang (69) for hydroentangled wood pulp wipes with 25% lyocell content.

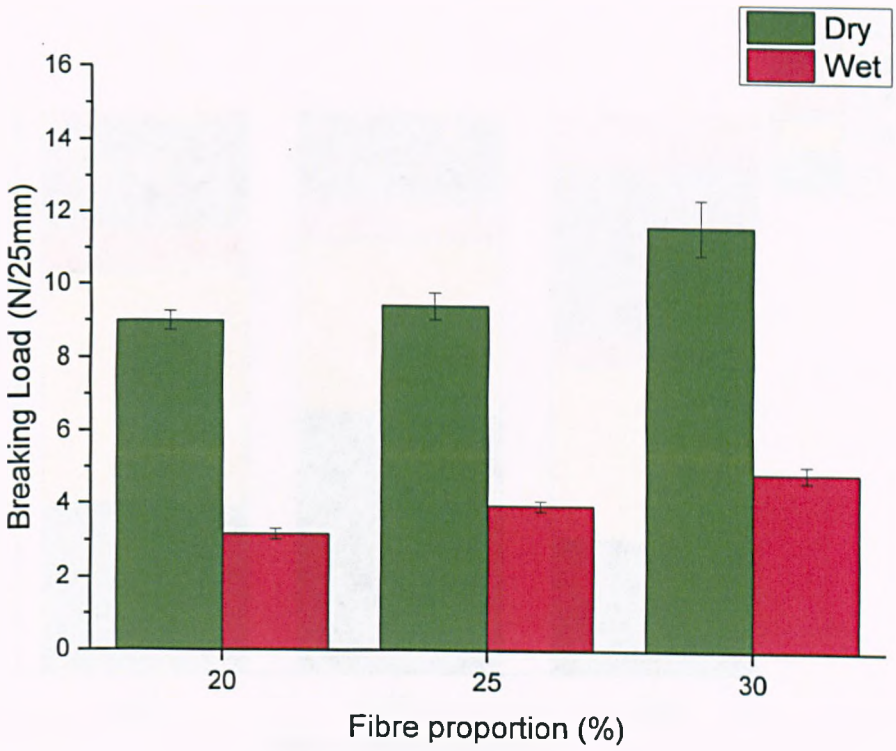


Figure 5.14 Influence of the proportion of Tencel A100 fibre (mean fibre length 10mm and linear density 1.4 dtex) on the MD tensile strength of wetlaid-hydroentangled fabrics containing wood pulp.

The corresponding dispersibility of the same wetlaid-hydroentangled fabrics is shown in Figure 5.15. The dispersibility of the fabrics containing 20% and 25% lyocell were similar with 98-100% of the fabric passing through the 12.5 mm screen after the test. However, when the fibre lyocell content increased to 30% the dispersibility markedly reduced, with only 90.2% passing through the 12.5 mm screen. This could be indicative of larger entangled entities being present in the water leaving the shake flask, rather than individualised fibres, preventing passage through the screens. It is probable that as the proportion of longer fibres in the blend increases, the number of fibres associated with individual entanglements will increase, reducing the likelihood of complete disintegration of the fabric and resulting in larger residues.

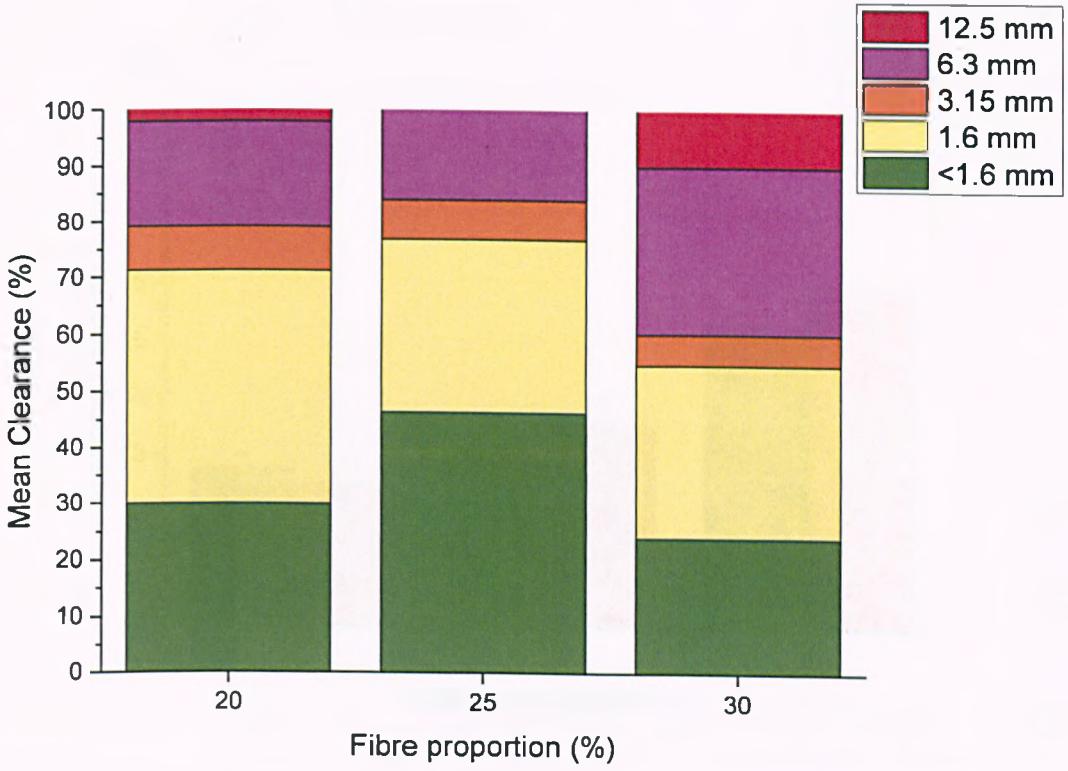


Figure 5.15. Influence of proportion of Tencel A100 fibre (mean fibre length 10mm and linear density 1.4 dtex) on the dispersibility of wetlaid-hydroentangled fabrics containing wood pulp

In a separate experiment, this time using airlaid-hydroentangled fabrics composed of wood pulp blended with 20%, 25% or 30% of Tencel A100 (1.4 dtex, 8 mm), the MD tensile strength in both the dry and wet state and dispersibility were determined as shown in Figure 5.16 and Figure 5.17 respectively. In these experiments, fabrics were hydroentangled using a specific energy of 1.192 $MJ.kg^{-1}$.

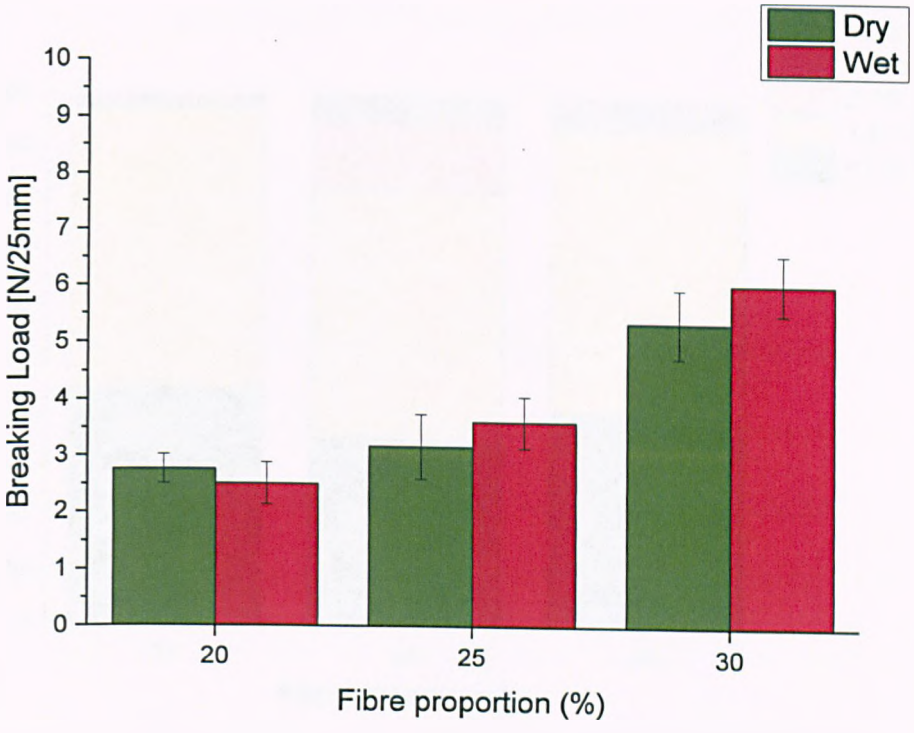


Figure 5.16. Influence of proportion of A100 Tencel (mean fibre length 10mm and linear density (1.4 dtex) on the MD tensile strength of airlaid-hydroentangled fabrics containing wood pulp

Despite the high wet tensile strength the airlaid-hydroentangled fabrics exhibited good dispersibility, with over 99% of the all the fabrics passing through the 12.5 mm screen and >94% passing through the 6.3 mm screen, shown in Figure 5.17. This finding is practically significant because it provides a potential route to address the persistent challenge of producing fabrics with adequate wet strength combined with excellent dispersibility.

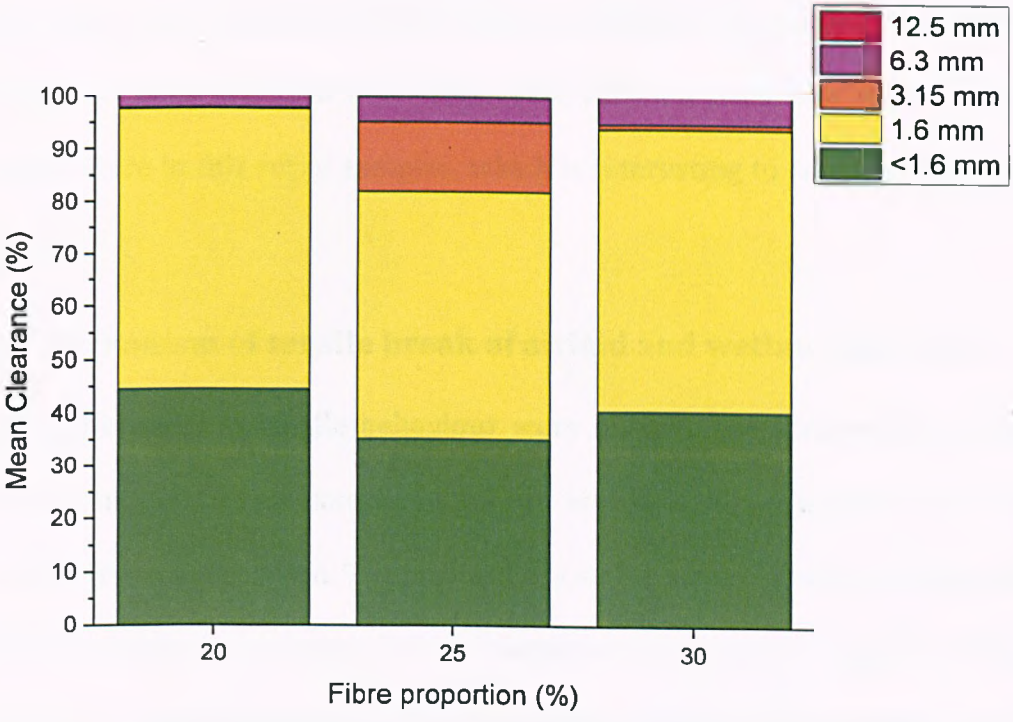


Figure 5.17 Influence of proportion of A100 (mean fibre length 10mm and linear density (1.4 dtex) on the dispersibility of airlaid-hydroentangled fabrics containing wood pulp

It had been previously assumed that airlaid-hydroentangled fabrics composed of wood pulp and regenerated cellulose short cut fibre would behave in a similar manner to wetlaid hydroentangled fabrics of the same composition, but this is not the case. Interestingly, with airlaid fabrics there is also the potential to introduce higher specific energy during hydroentangling, further increasing the potential to generate higher wet strengths, whilst not necessary substantially reducing dispersibility.

Referring to Figure 5.16 quite unexpected results were obtained in that the wet strength of the airlaid-hydroentangled fabrics was similar to or even greater than the dry strength. The reverse would normally be expected. The

experiment was repeated several times to confirm the results and the same finding was observed each time. This could reflect a particular mechanism of tensile failure in this set of samples, which is interesting to consider further in Section 5.4.

5.4 Mechanism of tensile break of airlaid and wetlaid materials

Major differences in tensile behaviour were observed in some of the airlaid-hydroentangled fabrics compared to the wetlaid-hydroentangled fabrics of identical fibre composition. The wet and dry stress-strain curves (tested in MD) of 80:20 pulp;lyocell 1.4 dtex, 10 mm blends are compared in Figure 5.18 and Figure 5.19. Both the airlaid and wetlaid fabrics were hydroentangled with an applied specific energy of 0.769 $MJ.kg^{-1}$. In general, wetlaid fabrics, of the same composition and hydroentangled using identical conditions, exhibited higher dry strengths and similar or lower wet strengths than the airlaid fabrics. Airlaid fabrics produced relatively low dry tensile strengths but similar, or in some cases (particularly at specific energies above 1.0 $MJ.kg^{-1}$), higher wet strengths. This is contrary to what would normally be expected.

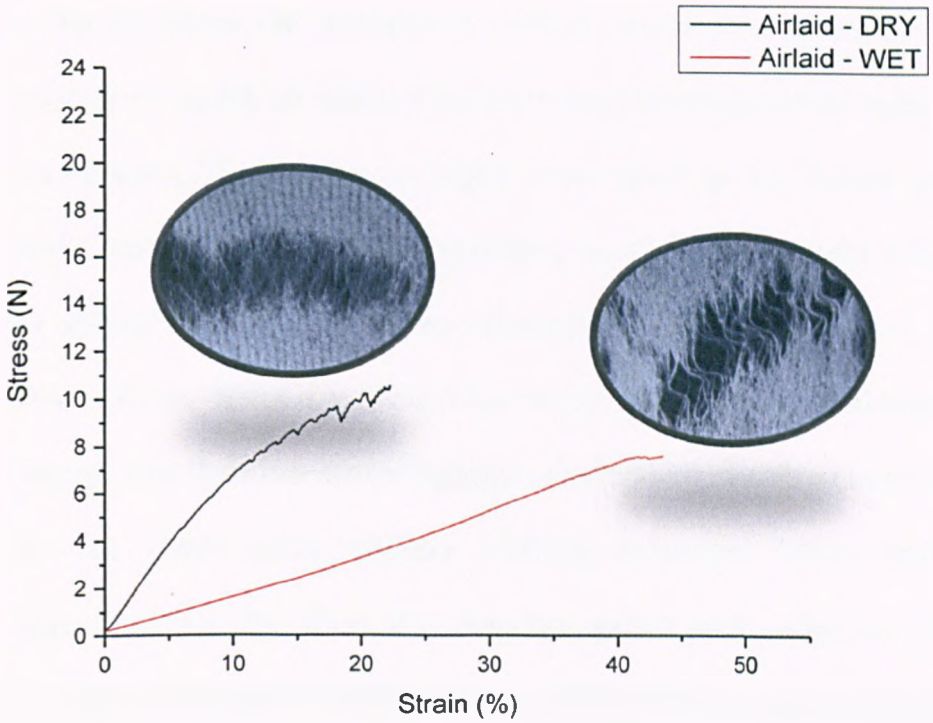


Figure 5.18. Stress-strain behaviour of airlaid-hydroentangled fabrics containing lyocell (mean fibre length 10mm and linear density 1.4 dtex) and wood pulp

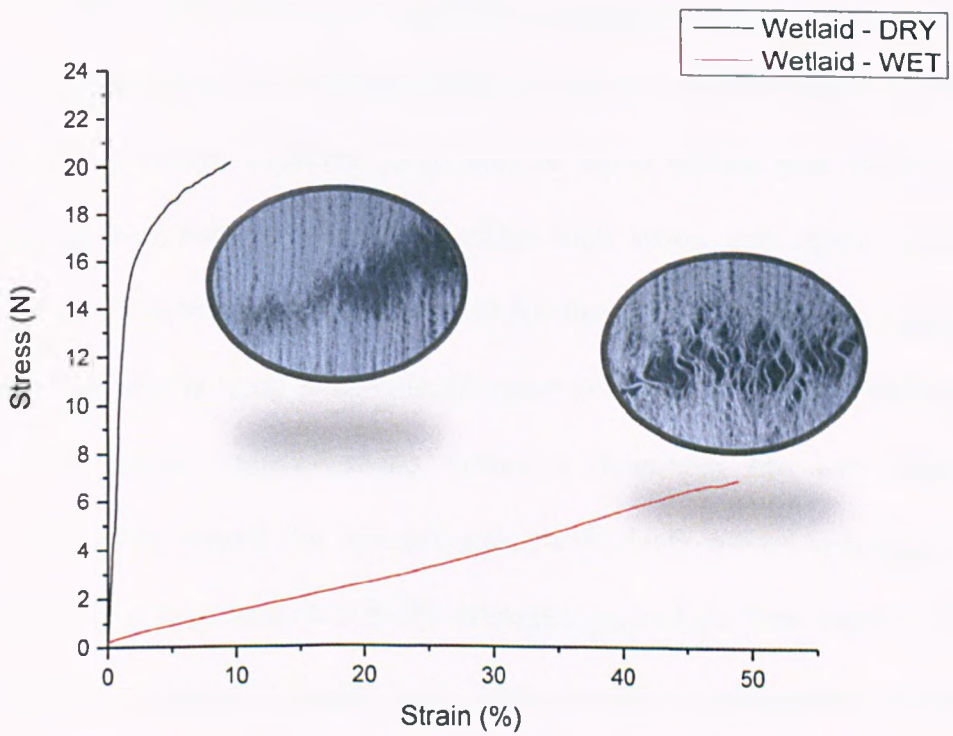


Figure 5.19. Stress-strain behaviour of wetlaid-hydroentangled fabrics containing lyocell (mean fibre length 10mm and linear density 1.4 dtex) and wood pulp

In the dry state, the strength of wetlaid nonwovens, as with dry paper, is determined by the strength of the fibres and by the bond strength at the fibre intersections. The bonding is largely determined by the friction generated by mechanical entanglement and hydrogen bonding. This would help to explain the differences between the dry strength of the hydroentangled wetlaid and airlaid fabrics. When dry wetlaid fabrics break, both fibres and bonds break as suggested by their low strain-high stress behaviour, resulting in brittle fracture. The dry airlaid fabric exhibits stick-slip behaviour before tensile failure, suggesting that the fibres are slipping against each other as well as fibre breakage resulting in ductile fracture. A study of wet paper webs by Tejado and van de Ven (224) supports this analysis in that the suggested mechanism is one of fibre entanglements and friction being the main contributors to wet tensile strength. In the wet state the airlaid and wetlaid fabrics show similar stress-strain behaviour, little fibre breakage is observed and the stress is generated by disentanglement of fibres, or groups of fibres sliding past one another. Wet tensile behaviour is characterised by high strain and relatively low stress. Similar tensile failure was observed for the dry airlaid fabrics, suggesting that friction arising from fibre entanglement is also largely responsible for tensile stress. Where entanglements exceed a threshold, the wet strength could conceivably exceed the dry strength, particularly where hydrogen bonding is limited such as in airlaid-hydroentangled materials. This helps to explain the behaviour shown in Figure 5.16. This unusual observation is unlikely to have been observed by other researchers because all commercial lines for flushable wet wipes are based on wetlaid web formation.

5.4.1 Numerical frequency of fibres in the blend

In relation to the regenerated cellulose fibre component in the blend with wood pulp, both the fibre length and the fibre fineness have an influence on the number of fibres present in a given weight of fabric. This is important because as fibre length or fibre fineness changes the total solid surface area of fibres available to form entanglements will vary. As the proportion of regenerated cellulose fibres in the blend increases from say 20-30% the total solid surface of fibres in the blend will increase, and the resultant increase in fibre-to-fibre frictional contact would be expected to lead to greater resistance to slippage and higher tensile strength. However, it cannot be assumed that increasing fibre length with fixed fibre fineness will have the same influence as decreasing the fibre fineness with a fixed fibre length. Nor can it be assumed that simply increasing the proportion of regenerated cellulose fibres in the blend will have the same influence as changing fibre dimensions. In terms of the wet MD tensile strength of the final fabric Figure 5.20 illustrates the effect of increasing the number of regenerated cellulose fibres in the blend by either, increasing the fibre length (left), decreasing the fibre fineness or increasing the proportion of regenerated cellulose fibres in the blend. The numbers of fibres per g of fabric was calculated using equation 5.1.

$$n.g^{-1} = \frac{\frac{10000}{linear\ density\ (dtex)}\ x\ ratio\ of\ regenerated\ cellulose}{fibre\ length\ (m)}$$

Equation 5.1

In this example, all the data relates to blends of wood pulp with lyocell in airlaid-hydroentangled fabrics. Fabrics were constructed from blends of wood pulp and lyocell and hydroentangled with a specific energy of 6.85 $MJ.kg^{-1}$. The

fibre length was varied between 6-10 mm, the linear density between 1.4-1.7 dtex and the relative proportion of lyocell between 20-30%.

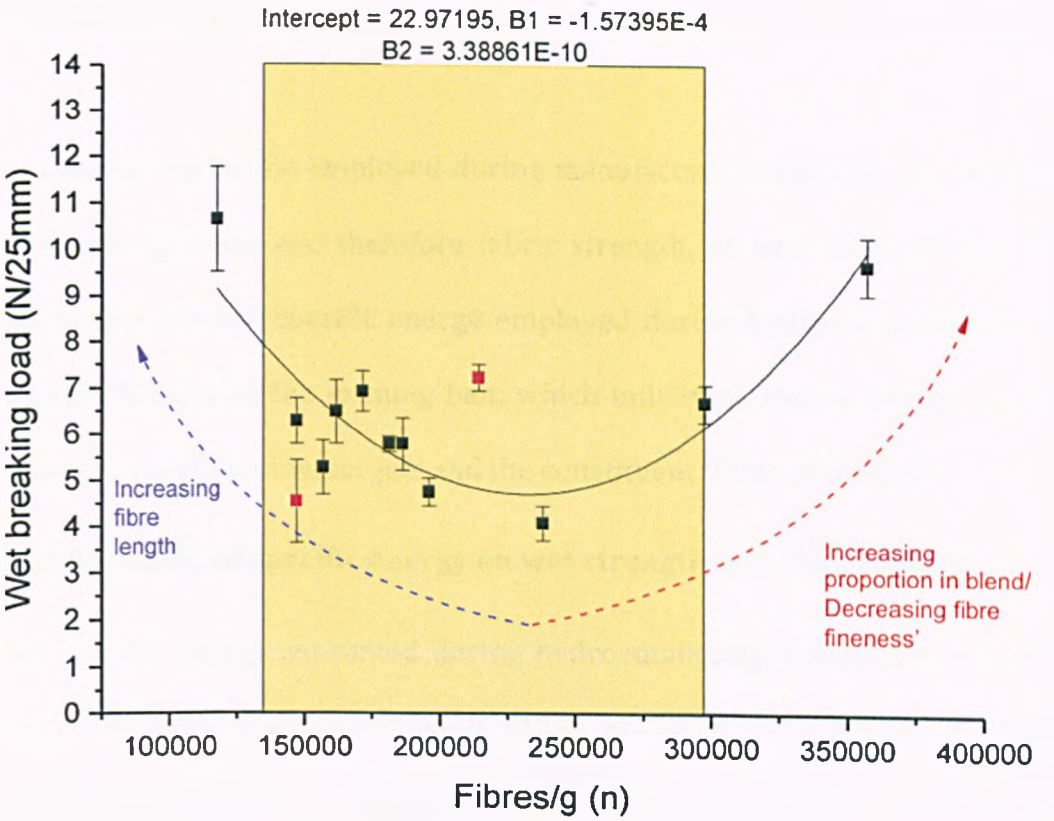


Figure 5.20. Number of fibres in wood pulp/lyocell airlaid-hydroentangled fabric in relation to changing fibre length or fibre fineness, and the influence on MD wet tensile strength

The relationship between the numbers of fibres per g of fabric and wet tensile strength is not linear. The lowest tensile strength in these data was obtained for at 2.25 x 10^5 fibres/g, which relates to a fabric containing 20% of 6 mm lyocell fibre. Increasing the fibre length reduces the number of fibres per g but results in an increase in wet strength. Increasing the proportion of lyocell fibre in the blend or increasing the fineness leads to an increase in the number of fibres per g beyond 2.25 x 10^5 fibres/g, which also increases the wet strength. The fabric containing approximately 3.5 x10^5 per g is a fabric composed of 30% 6 mm

lyocell. Accordingly, to maximise the wet tensile strength of the fabric, increasing the fibre length and the proportion of lyocell in the blend are plausible strategies.

Various means can be employed during manufacture of the fabric to influence fibre entanglement and therefore fabric strength, as well dispersibility. Two key factors are the specific energy employed during hydroentanglement and the specification of the forming belt, which influences kinetic energy transfer between the incident water jets and the constituent fibres of the web.

5.4.2 Influence of specific energy on wet strength and dispersibility

The specific energy consumed during hydroentangling is known to influence fabric strength. Mao and Russell (125) observed in a study of carded-hydroentangled fabrics composed of viscose fibres, that fabric tensile strength increases rapidly above a certain energy threshold to a peak value before levelling. Further increases in specific energy can eventually result in structural degradation leading to a decrease in tensile strength. Zheng et al (150) reported a similar relationship of increasing tensile strength with specific energy up to about 12 $MJ.kg^{-1}$. Between 12-45 $MJ.kg^{-1}$ no further increases in tensile strength were observed. Since specific energy influences the degree of fibre entanglement generated during bonding of the web, it can also be expected to influence dispersibility. Apart from limited data published in the patent literature (59) there is a paucity of academic research work in this area.

The MD wet tensile strength of both airlaid-hydroentangled and wetlaid-hydroentangled fabrics was examined using different specific energies. The manufacturing conditions for each fabric are given in Section 3.2. The purpose was not to directly compare the absolute values obtained for the airlaid and wetlaid fabrics, but to understand if overall trends in the data were consistent. Both sets of fabric were constructed from 80% wood pulp and 20% lyocell fibre. The fibre lengths differed, with the airlaid fabric composed of 1.7 dtex, 6 mm length fibre and the wetlaid made from 1.7 dtex, 8 mm length fibre. The specific energy inputted with the airlaid web was much higher (up to 6.85 $MJ.kg^{-1}$) compared to the wetlaid (up to 0.769 $MJ.kg^{-1}$). The wetlaid fabrics could not be bonded with such high specific energies because of the water pressure limitations of the pilot plant, and also because the wetlaid web was found to structurally disintegrate at pressures approaching 1 $MJ.kg^{-1}$. The relationship between specific energy and specific wet breaking load for the airlaid and wetlaid fabrics are shown in Figure 5.21 and Figure 5.22 respectively.

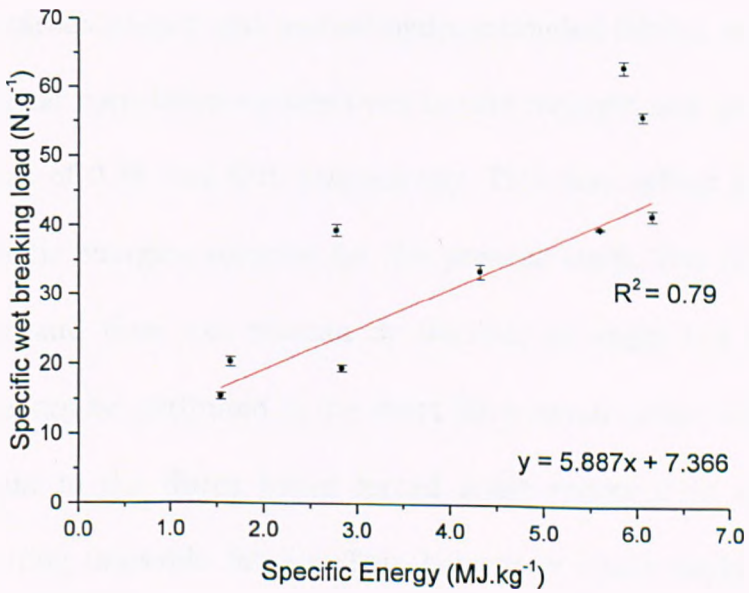


Figure 5.21 Relationship between specific MD wet breaking load and increasing specific energy for airlaid hydroentangled pulp-lyocell (1.7 mm, 6mm) fabrics

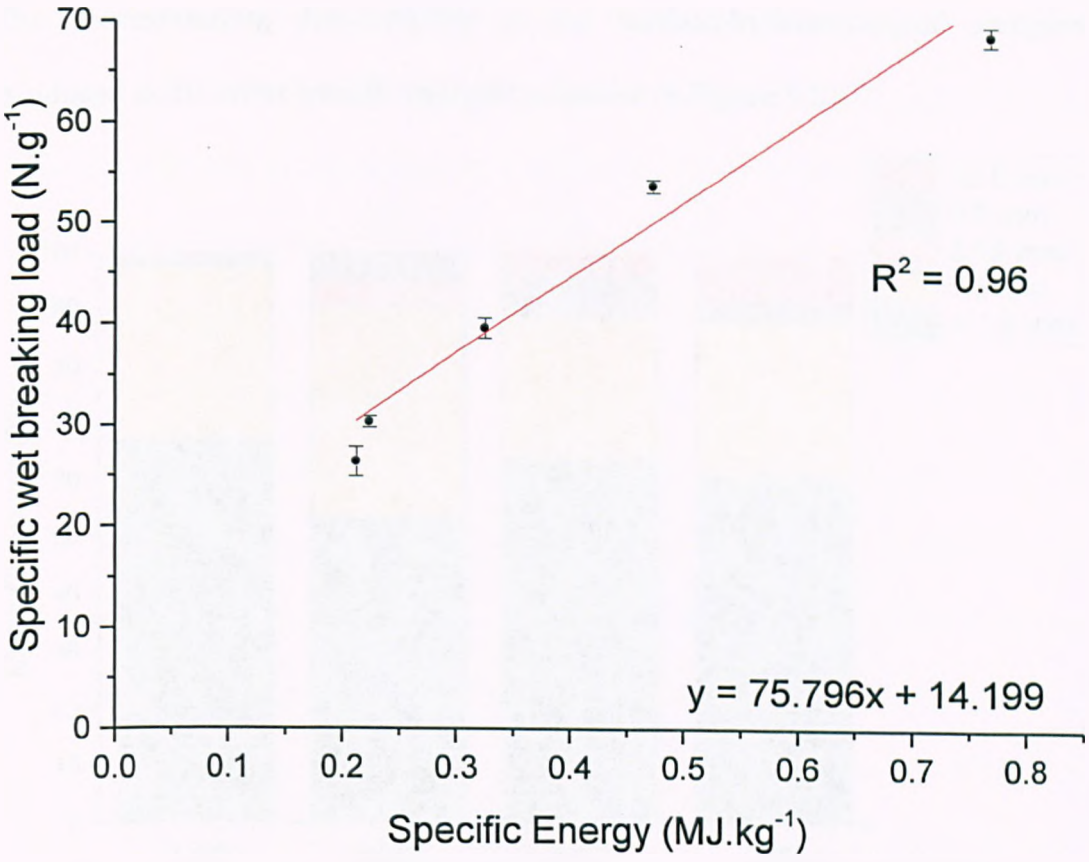


Figure 5.22. Relationship between specific MD wet breaking load and increasing specific energy for hydroentangled pulp-lyocell (1.7 mm, 6mm) wetlaid fabrics

Unlike the carded materials studied by Mao and Russell (125) and Zheng (253), the airlaid-hydroentangled and wetlaid-hydroentangled fabrics studied herein exhibited a linear correlation between wet tensile strength and specific energy, with R^2 values of 0.79 and 0.96 respectively. This may reflect the narrower range of specific energies selected for the present work. The relationship is purely linear and does not plateau or decline, as suggested by previous research. This can be attributed to the short fibre construction; higher applied energies result in the fibres being forced apart rather than causing fibre damage, creating unusable fabrics. This behaviour could explain increased variation observed in the airlaid fabric data.

The corresponding dispersibility of the wetlaid-hydroentangled samples produced at different specific energies is shown in Figure 5.23.

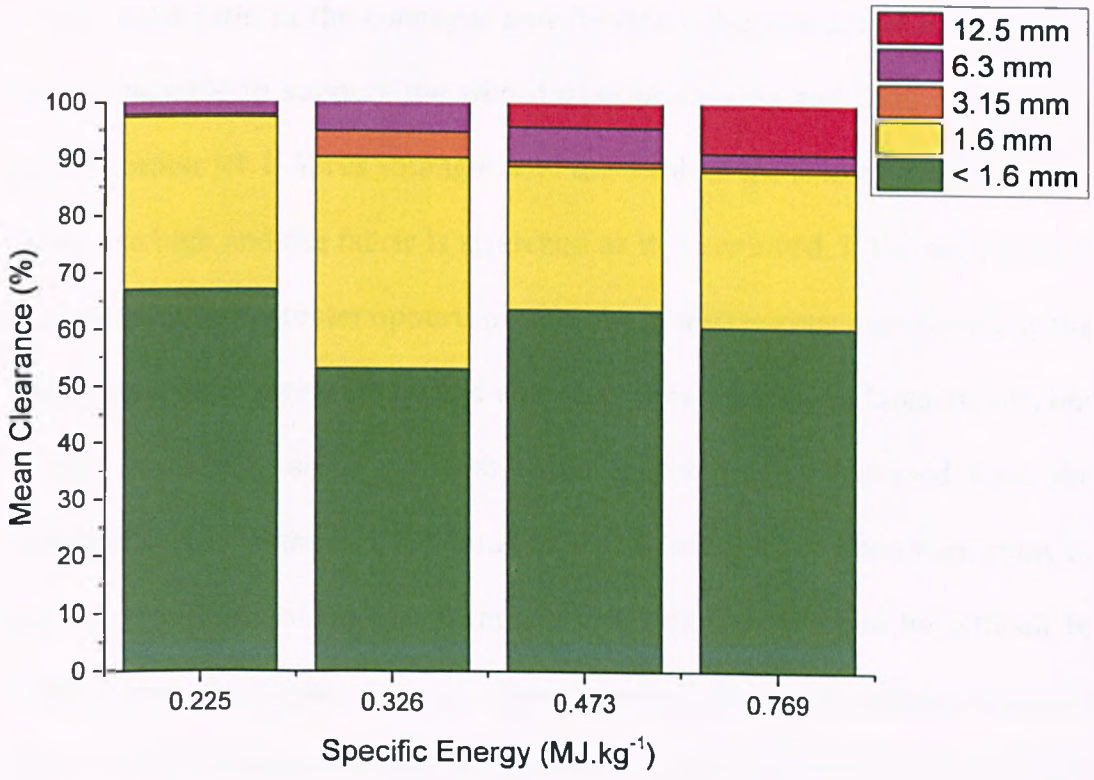


Figure 5.23. Effect of specific energy on the dispersibility of wetlaid-hydroentangled wood 80:20 pulp-lyocell (8 mm; 1.4 dtex) wipes

In Figure 5.23 it is evident that dispersibility was negatively affected by increasing the specific energy used to manufacture the base fabric, as indicated by the progressive reduction in mean clearance of the 12.5 mm screen. This is reasonable given that the specific energy will tend to increase fibre entanglement in the fabric, and increase the likelihood of larger entangled residues in the water as the structure disintegrates.

5.4.3 Effect of forming belt open area

The mesh size of the forming belt in hydroentanglement is known to influence the strength of wetlaid fabrics. Mesh size characterises the size of the openings

in the woven conveyor belt used in the process and is defined as the number of openings per unit width (n. 2.54 cm^{-1}). Clearly, the mesh size influences the void to solid ratio in the conveyor and therefore the amount of solid surface that is available to support the web during processing and interact with the incident water jet. If fibres entangle with the mesh of the conveyor then peeling forces are high and the fabric is stretched as it is removed. If the open area is small then there is greater opportunity for the kinetic energy transferred by the water jets to intensively rotate and entwine fibres, creating entanglements, but energy losses may occur if excess water is not quickly removed from the conveyor surface. Gahide (152) found that if the mesh is too open then many of the shorter fibres can be lost from the web and the web can be difficult to remove from the screen. Use of a finer screen (100 mesh) enabled coherent fabrics to be produced but only if their basis weights exceeded 60 $g.m^{-2}$ could they be removed from the conveyor at the highest hydroentangling water pressures (up to 2.0 $hp.hr.lb^{-1}$ or 11.84 $MJ.kg^{-1}$).

Experimental airlaid-hydroentangled fabrics were constructed from 80% wood pulp and 20% lyocell (6 mm, 1.7 dtex). Fabrics were manufactured using the method described in section 3.2. For all other airlaid-hydroentangled fabrics in this work the mesh size was kept constant at 70 mesh (33.8% open area) as detailed in 3.2.3.1. For these experiments, the open area of the conveyor was varied between 31.4 - 45.6% (30-120 mesh; 0.595–0.125 mm openings). The specific energy was kept constant at 0.72 $MJ.kg^{-1}$. The wet and dry MD tensile strengths of the resultant fabrics are shown in Figure 5.24.

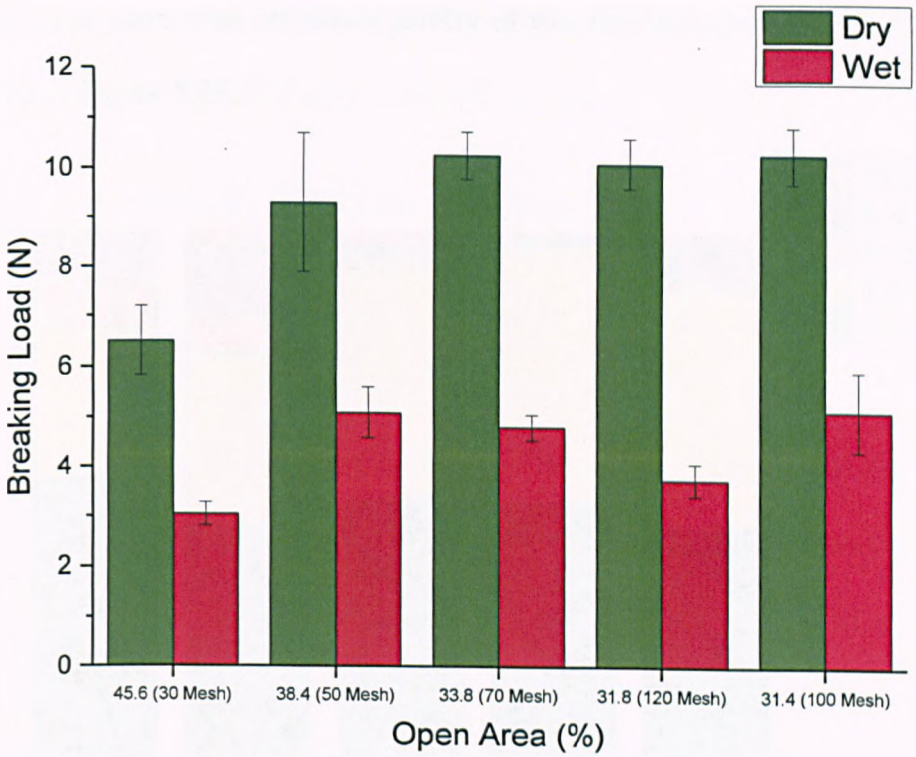


Figure 5.24. Influence of conveyor screen openness on the MD tensile strength of 80% wood pulp and 20% lyocell (6 mm, 1.7 dtex) airlaid-hydroentangled fabrics

Gahide (152) observed that hydroentangling on the most open meshes resulted in reduced tensile strength because of fibre losses through the conveyor. The present study confirmed that reducing the open area to ≤ 38.4% open area (50 mesh) resulted in less fibre loss and produced the highest dry tensile strengths. There was little difference in dry fabric tensile strengths using conveyors with mesh sizes from 31.8-45.6% open area (50-100 mesh). Previously, Andersen (153) has recommended conveyors of 38-58 mesh size as the optimum for hydroentangling, but the present work suggests that there may be a higher upper limit. Using the smallest open area conveyor (31.8%; 120 mesh) a low tensile strength was observed due to inadequate water removal from the conveyor surface during hydroentanglement. The corresponding influence of

the conveyor open area on dispersibility of the airlaid-hydroentangled fabrics is shown in Figure 5.25.

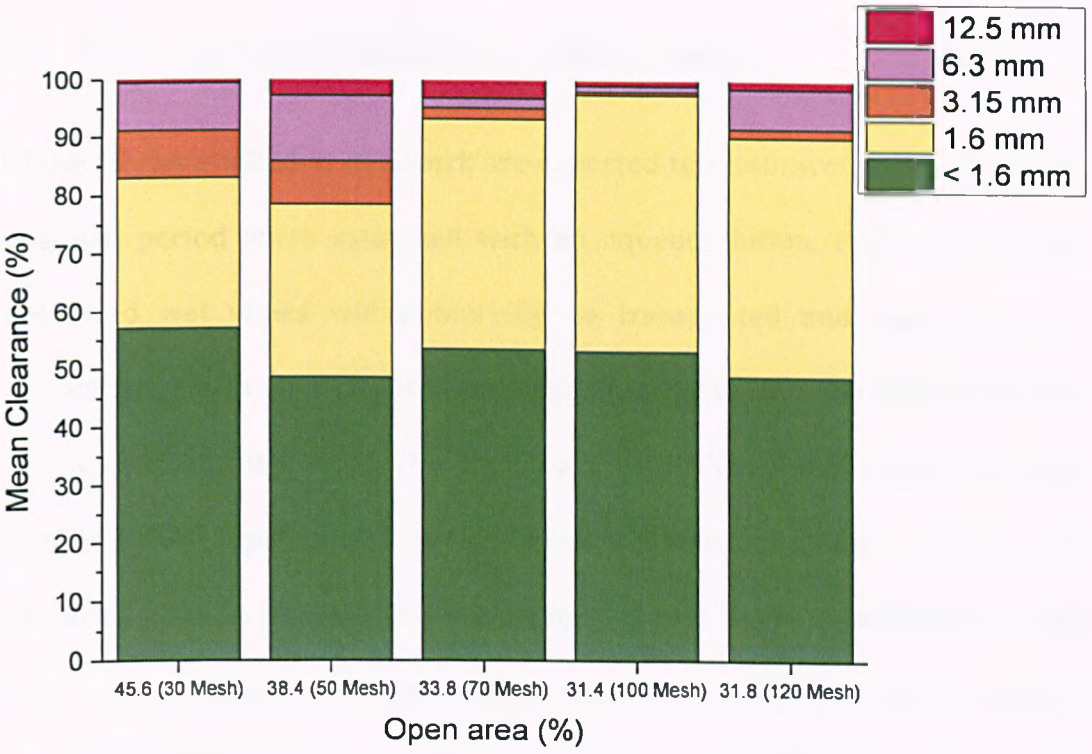


Figure 5.25. Influence of screen openness on dispersibility of airlaid-hydroentangled fabrics constructed from 80% wood pulp and 20% lyocell (6 mm, 1.7 dtex)

Unexpectedly, screens with highest open area result in the lowest dispersibility performance exhibiting the lowest mean clearance for screens sizes 1.6 mm and above, which does not correlate with the tensile strength. The reasons for this are not well understood but it is possible that removal of short fibre through the more open conveyor meshes means that there will be fewer short pulp fibres in the final fabric. Therefore, the proportion of long regenerated fibres in the fabric will slightly increase, negatively effecting the clearance value. Additionally, preferential removal of short fibres may produce localised areas of intensely entangled longer fibres, which do not disentangle easily.

Decreasing the openness of the conveyor resulted in less short fibre loss during processing, and more a homogenous fabric structure.

5.5 Time-dependent effects on tensile strength

All the fabrics studied in this work are expected to retain wet strength over an extended period when saturated with an aqueous lotion. Prior to use, pre-moistened wet wipes will potentially be transported and then stored in packaging for many months. Additionally, after disposal in the toilet fabrics do not immediately transit to the treatment plant. They can spend extended periods in the pipeline and sewer network before eventually reaching the treatment plant. A product that breaks up within 6 hours is considered not to cause any blockages to sewer pumps (14). During this period the wipe is saturated with wastewater, which in addition to washing off the lotion could also potentially trigger disintegration of the wipe, reducing its strength. An experiment was conducted to understand how fabric strength might change over as a function of time in the wet state, at full absorbent capacity, as would likely be encountered after disposal.

The experiment was conducted using two wetlaid-hydroentangled fabrics both composed of 75:25 woodpulp and lyocell or Tencel A100 (1.4 dtex, 10 mm) and loaded with lotion. The MD and CD tensile strength of the fabrics was tested after immersion in tap water for periods up to 6 hr without agitation. One fabric was comprised of lyocell and the other from Tencel A100. These fibres are known to have slightly different mechanical properties and swelling behaviour as a result of crosslinking treatment and therefore, it was reasoned

that disentangling behaviour might differ. Each fabric was bonded at 0.769 $MJ.kg^{-1}$ specific energy. The fabrics were tested at full maximum absorption capacity, after immersion, each sample was allowed to drip dry for 2 minutes before testing using a tensile testing machine with a constant rate of extension. The relationship between wet tensile strength and immersion time for the wood pulp-lyocell fabrics is shown in Figure 5.26 and Figure 5.27.

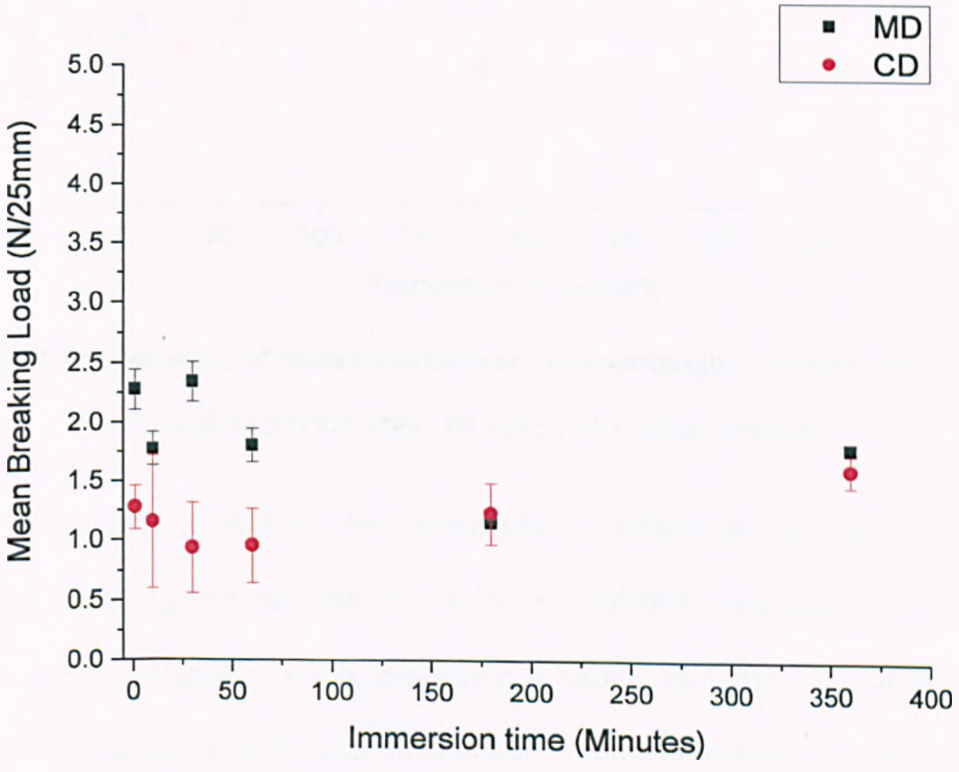


Figure 5.26. Influence of immersion time on hydroentangled wetlaid wood pulp-lyocell (1.4 dtex, 10 mm) wet tensile strength

It is evident in Figure 5.26 and Figure 5.27 that the tensile strength of the fabrics was not significantly affected by immersion time. Thus, any reduction in fabric strength is likely to occur immediately after saturation, with little time dependent change, even up to periods over 6 hr. No significant variation in this trend was evident for the different specifications of fibre (Tencel A100 and standard lyocell).

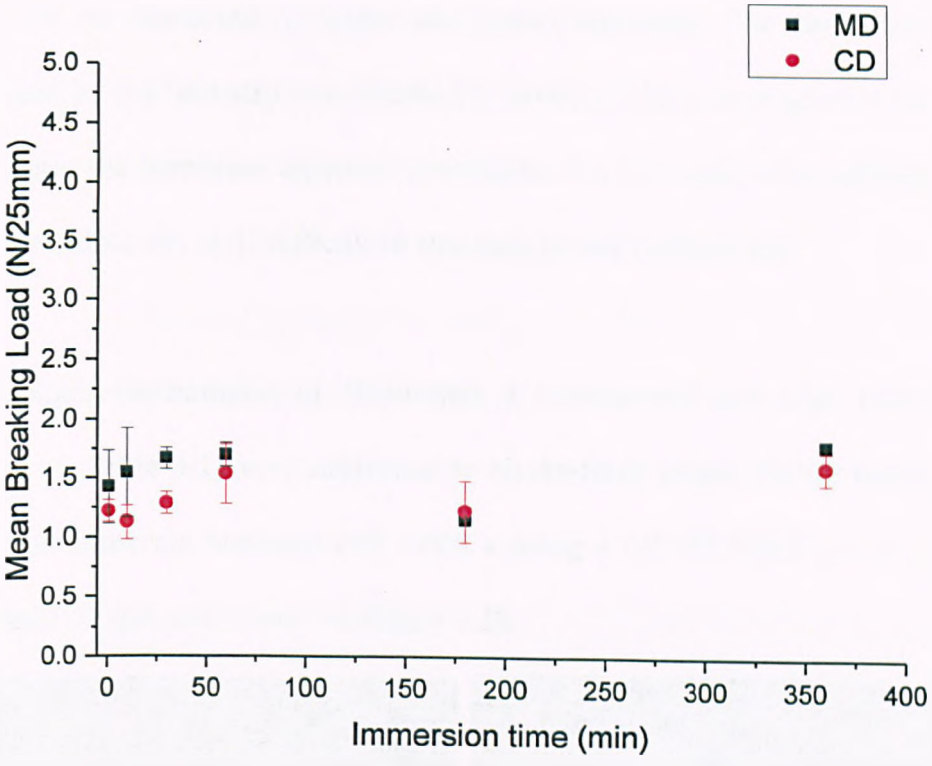


Figure 5.27. Influence of immersion time on hydroentangled wetlaid wood pulp-Tencel A100 (1.4 dtex, 10 mm) wet tensile strength

Thus, there was no evidence that dispersibility is likely to increase over time due to decreasing wet strength. Of course, the addition of mechanical agitation could also be influential, but in practice it is known that after clearance of the toilet bowl, wipes can remain in the pipeline without significant agitation as the excess water drains away after each flush. It has been shown experimentally that multiple flushes (>3) are required to clear a product from a 16 m household drainline to the main sewer pipe (255).

5.6 Mechanisms of dispersibility

The mechanism of dispersion for short-fibre hydroentangled fabrics is not well understood. After a wet wipe is discarded in the toilet it enters a turbulent aqueous environment, which also acts as transport medium. Any residual lotion on the fabric is likely to be removed and hydrogen bonding between cellulose

fibres will be disrupted as water absorption increases. The shake-flask test developed by the industry and detailed in section 3.3.1 was originally designed to simulate the turbulent aqueous conditions of a domestic toilet although the entire drainline circuit is difficult to simulate in one unified test.

To elucidate mechanisms of dispersion, a commercial wet wipe (Carrefour, detailed in Table 4.1) was subjected to shake-flask dispersibility testing and imaged at intervals between 600-4200 s using a JVC KY-F550 video camera. Timelapse images are shown in Figure 5.28.

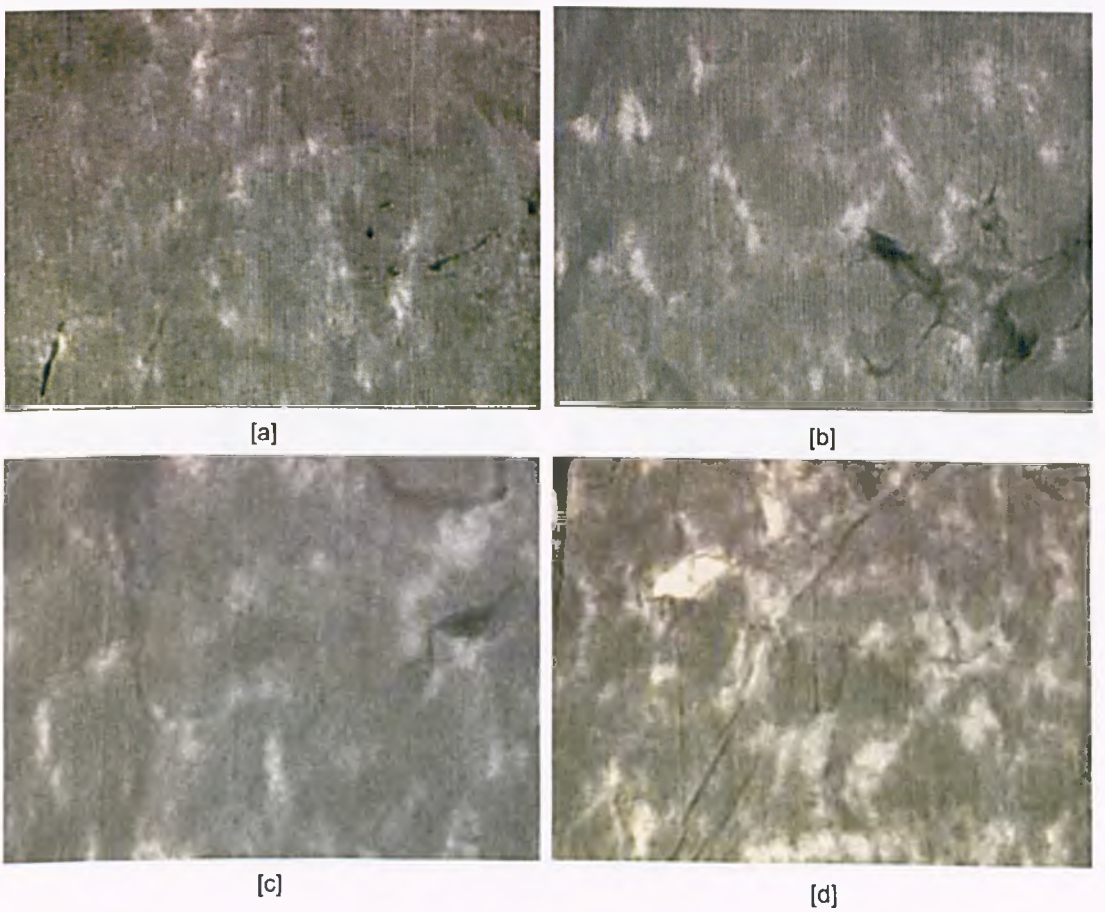


Figure 5.28. Timelapse images of wipe disintegration of a commercial flushable wipe in the shake-flask test (a) 600 s (b) 1200 s (c) 2400 s (d) 4200 s

The agitation in the shake-flask is sufficient to initiate break up of the wipe after just 600 s. As the wipe is subjected to further treatment the wipe continues to break up, with peak disintegration occurring after 4200 s. Note that the wipe does not break up uniformly but fragments in discrete areas. The extent of fragmentation increases as testing time increases. Fragmented areas were carefully removed from the shake flask, air dried in tensionless conditions and then analysed using optical microscopy (Motic BA300) and SEM to identify the mode of breakage, shown in Figure 5.29.

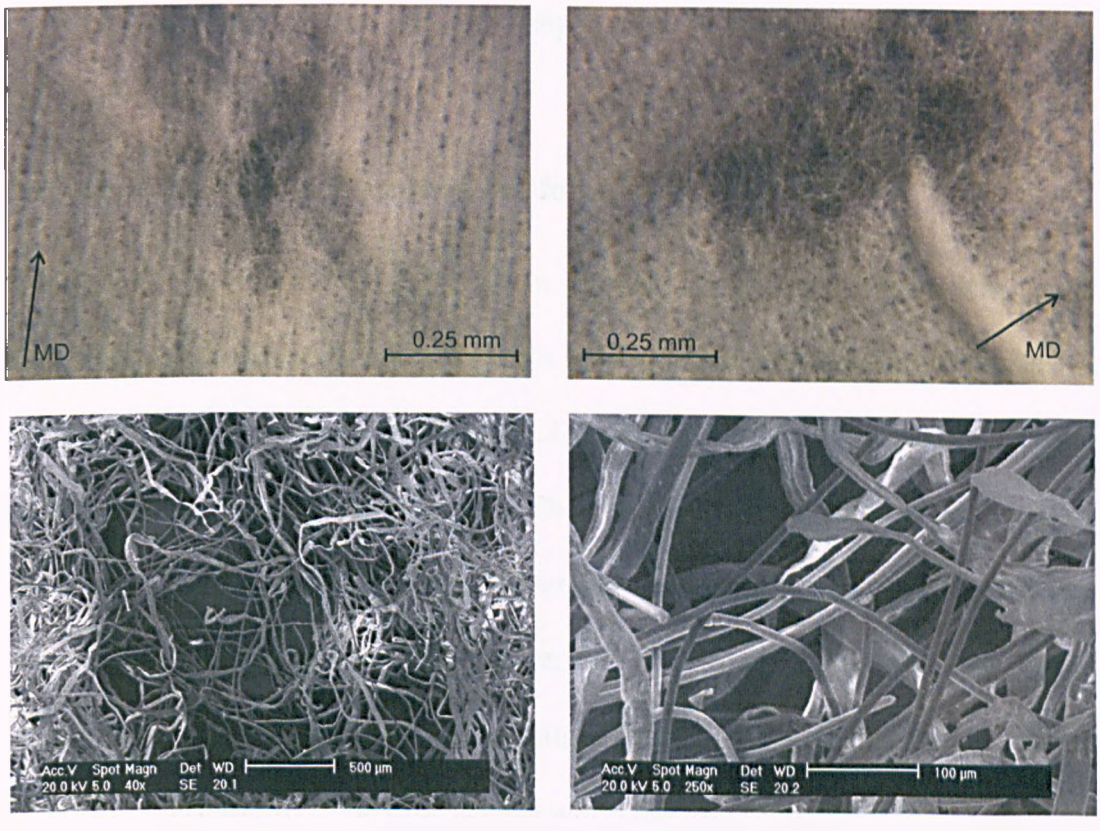


Figure 5.29. Images of Carrefour commercial wipe comprised of wood pulp and lyocell (60 g.m^{-2}) at the break-up interface after shake flask testing for 4200 s

Careful inspection of areas in which fragmentation had commenced revealed no evidence of fibre breakage, which given the low magnitude of the hydraulic forces during shake flask agitation was expected. Initiation of fragmentation

appeared to be the result of localised slippage of fibres and depletion of fibre-to-fibre frictional contact points. Areas in which there was a high localised concentration of wood pulp rather than lyocell were more susceptible to fibre slippage, initiating fragmentation. In this regard, wet fibre-fibre sliding friction could also be critical in determining dispersibility behaviour. This mechanism reinforces the importance of fibre length and the effect of blend proportions on the degree of disintegration that is observed in shake flask testing. As slippage between fibres initiates, not only will short fibres be entangled with fewer surrounding fibres but also complete separation will occur within a very short displacement distance.

5.6.1 Measurement of fibre cohesive force

Given the importance of slippage in the disintegration mechanism, it is instructive to examine the stress-strain behaviour of pre-moistened fabrics. A fibre pull out test detailed in section 3.3.7 was devised to evaluate the relative sliding friction of the fibres in a wipe. The cohesive force is defined as the force required to bring about relative movement of fibres in the web (248). For dispersibility this is particularly important in the saturated state. Previous attempts have been made to remove single fibres from hydroentangled fabrics (248) but were found to be impractical when dealing with short-fibre cellulosic materials. The modified approach adopted herein measures the force required to remove a group of fibres in the form of a 5 mm wide tab at one end of the test specimen. The results of this procedure give a useful insight in to how fabrics begin to disintegrate when wet, over very short displacement distances.

For these experiments, two sets of wetlaid-hydroentangled fabrics were produced containing 80:20 wood pulp and lyocell (standard and Tencel A100, 1.4 dtex, 10 mm). Each was bonded at 0.72 $MJ.kg^{-1}$ of specific energy. The wet cohesion forces were measured in both the wet (in tap water) and the dry states in the MD and CD. Five repeats per fabric for MD and CD dry cohesion force are shown in Figure 5.30, Figure 5.31, Figure 5.32 and Figure 5.33.

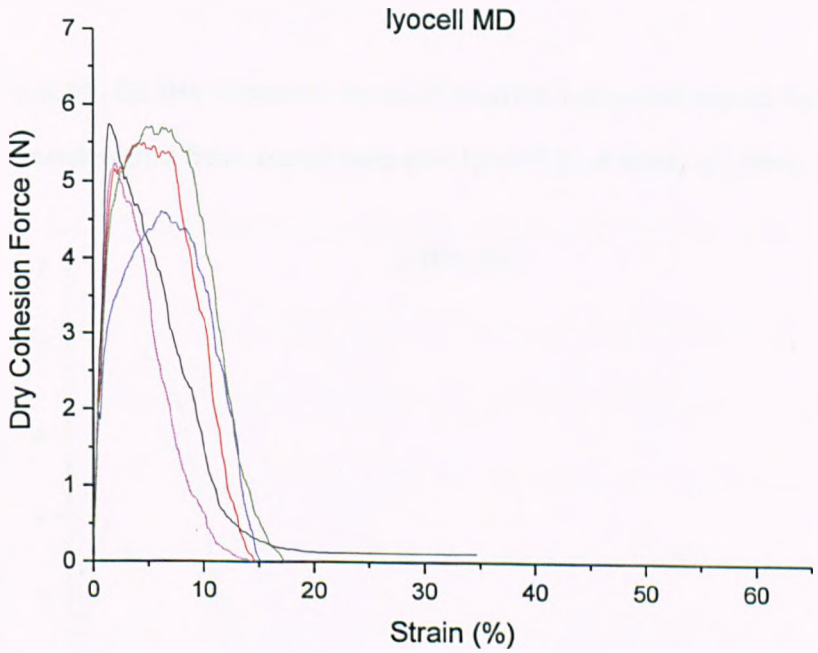


Figure 5.30. MD Dry cohesion force of wetlaid-hydroentangled fabrics constructed from wood pulp and lyocell (1.4 dtex, 10 mm)

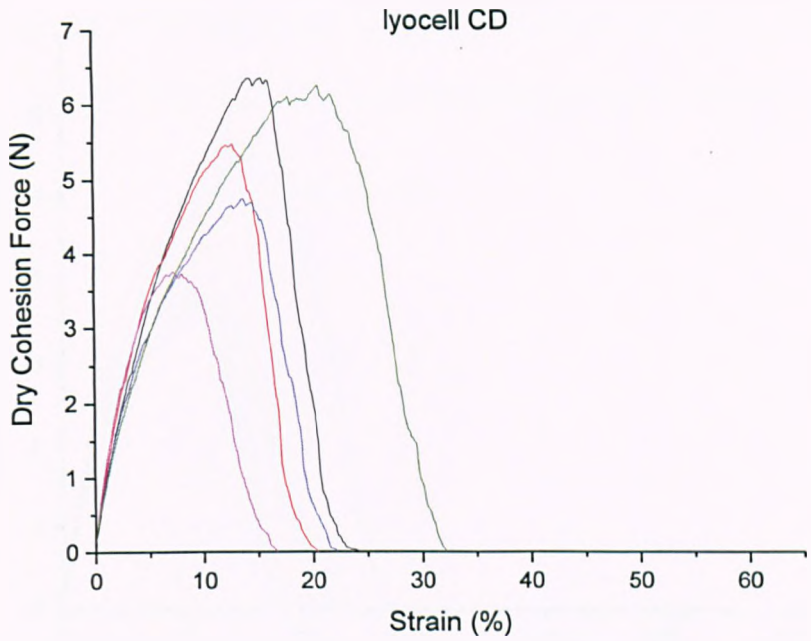


Figure 5.31. CD Dry cohesion force of wetlaid-hydroentangled fabrics constructed from wood pulp and lyocell (1.4 dtex, 10 mm)

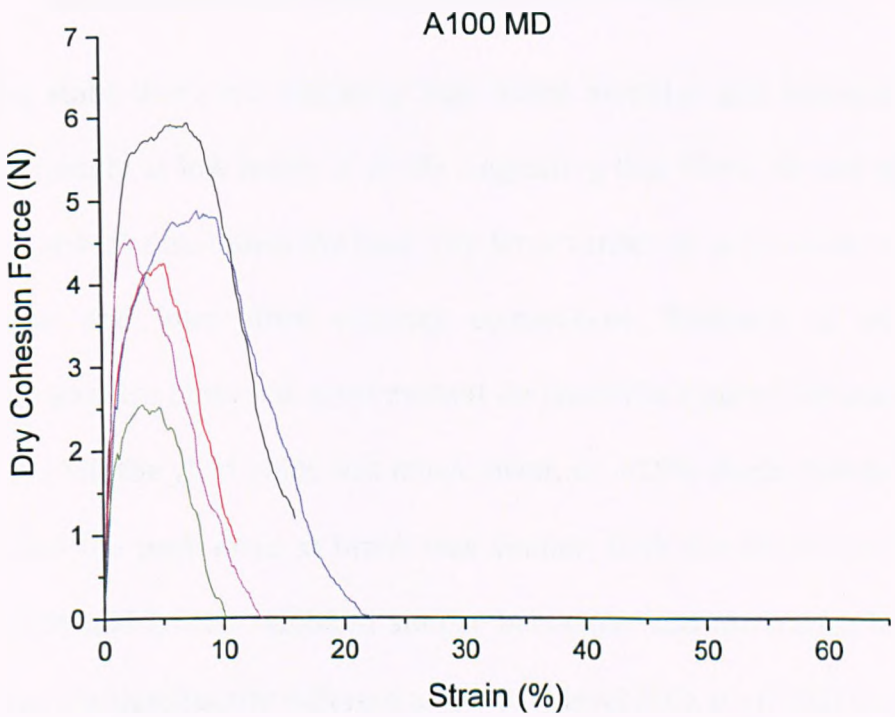


Figure 5.32. MD Dry cohesion force of wetlaid-hydroentangled fabrics constructed from wood pulp and A100 (1.4 dtex, 10 mm)

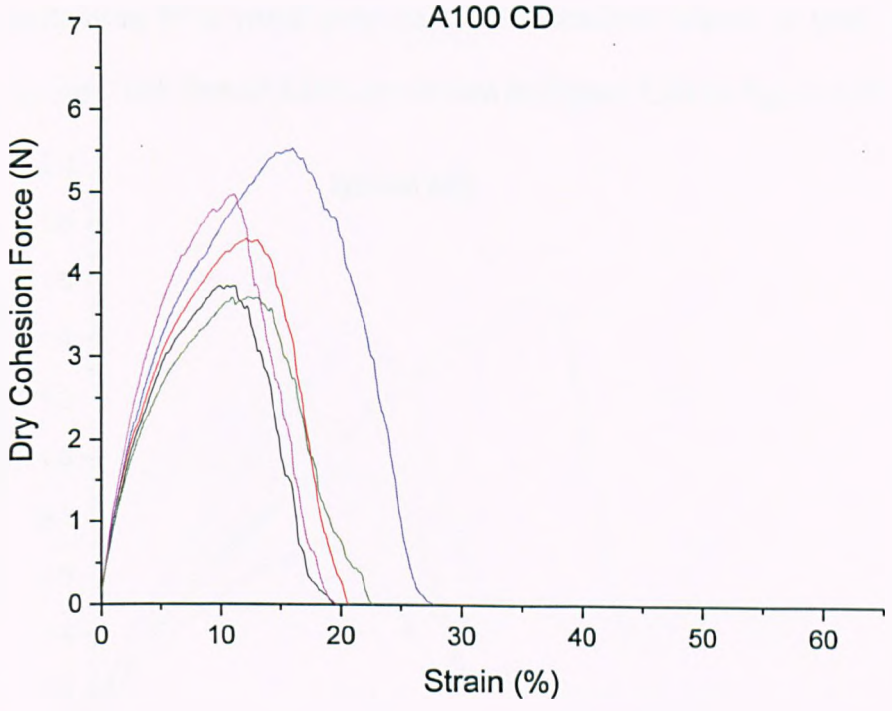


Figure 5.33. CD Dry cohesion force of wetlaid-hydroentangled fabrics constructed from wood pulp and A100 (1.4 dtex, 10 mm)

In the dry state, there is a relatively high initial modulus and cohesion force increases rapidly at low levels of strain suggesting that fibres do not slip and the fibre network distributes the load. The force continues to increase until the yield point and inter fibre slippage commences. Evidence of stick-slip behaviour was also observed, most evident for lyocell in Figure 5.30 and Figure 5.31. In the MD the yield point was much lower, ca. <10% strain that in the CD (<30%), but the peak force at break was similar. Both the fabrics containing Tencel A100 and lyocell exhibited similar behaviour and the means breaking loads were not significantly different at the 0.05 level (MD, $p = 0.305$) and (CD, $p = 0.204$).

The wet cohesion behaviour, which is more relevant to the conditions present in the shake flask, was quite different in both fabrics. The wet curves for the

fabrics containing 80% wood pulp and 20% standard lyocell as well as 80% wood pulp and 20% Tencel A100 are shown in Figure 5.34 to Figure 5.37.

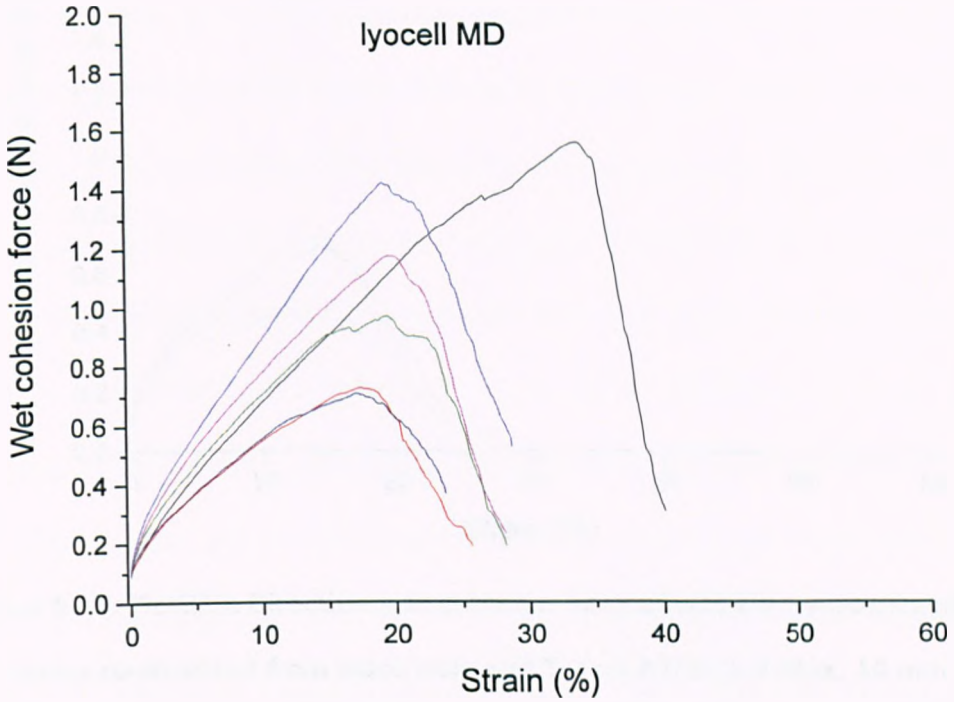


Figure 5.34. Machine direction wet cohesion force of wetlaid-hydroentangled fabrics constructed from wood pulp and lyocell (1.4 dtex, 10 mm)

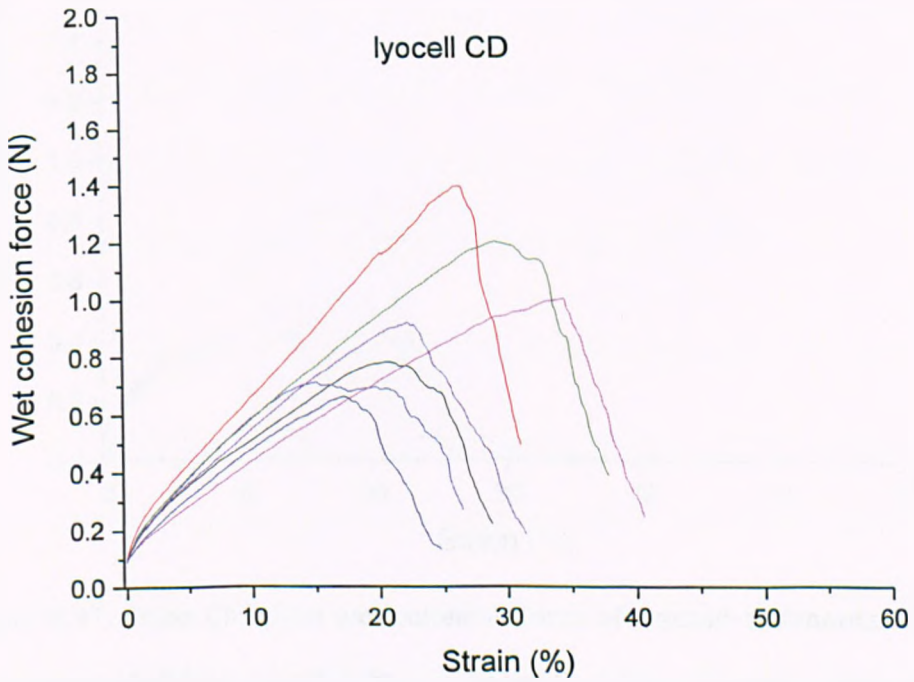


Figure 5.35. Cross Direction wet cohesion force of wetlaid-hydroentangled fabrics constructed from wood pulp and lyocell (1.4 dtex, 10 mm)

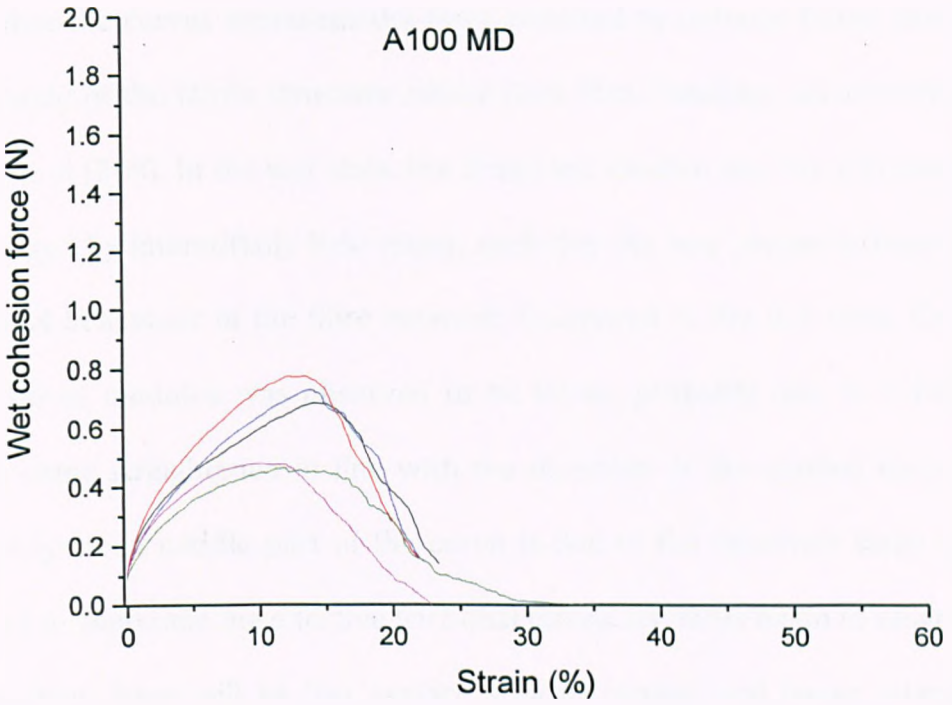


Figure 5.36. Machine Direction wet cohesion force of wetlaid-hydroentangled fabrics constructed from wood pulp and Tencel A100 (1.4 dtex, 10 mm)

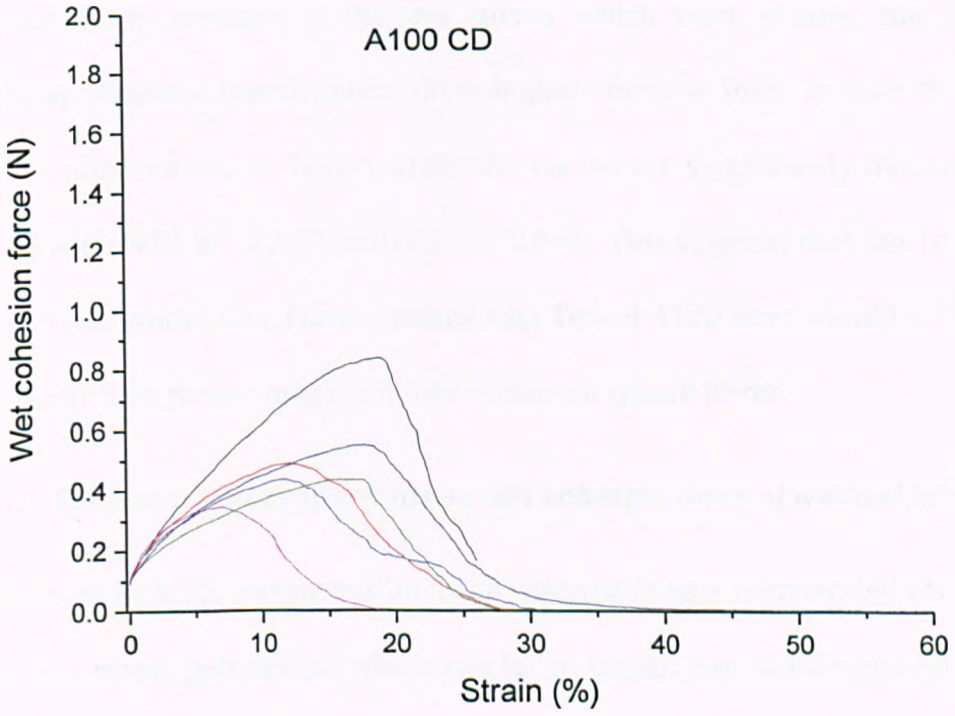


Figure 5.37. Cross Direction wet cohesion force of wetlaid-hydroentangled fabrics constructed from wood pulp and lyocell (1.4 dtex, 10 mm) – Tencel A100 CD showing lower force compared to lyocell

Note that the curves represent the force required to pull-out fibres from the main body of the fabric structure rather than fibre breakage, as identified by Wang et al (248). In the wet state, the fibres are swollen and the surfaces may be bridged by interstitially held water, such that the two phases influence the frictional behaviour of the fibre network. Compared to the dry state, the wet state initial modulus was observed to be lower, probably due to individual fibres being straightened in line with the direction of the applied force. The relatively steep middle part of the curve is due to the relatively large forces needed to overcome the effective frictional forces. As fibres begin to move over each other, there will be less surface area in contact and fewer inter fibre contact points, reducing the force in the third part of the curve. This tensile response is similar to that observed in card and drawframe slivers (256). Interestingly, in contrast to the dry curves which were similar, the fabric containing standard lyocell fibres show higher cohesive force in both the MD and CD compared to the Tencel A100, the means are significantly different at the 0.05 level (MD, $p = 0.023$) and (CD, $p = 0.006$). This suggests that due to their wet frictional properties, fabrics comprising Tencel A100 fibre should disperse more easily than those comprised from standard lyocell fibres.

5.6.1.1 Effect of blend proportions on wet cohesion force of wetlaid fabrics

As observed in 5.3.2, increasing the proportion of longer regenerated cellulose fibres in a wood pulp-lyocell blend results in higher wet tensile strength but negatively affects dispersibility. The wet cohesion force of wetlaid-hydroentangled wood pulp/Tencel A100 (1.4 dtex; 10 mm) in which the

proportion of Tencel A100 in the blend is systematically varied is reported in Figure 5.38. All fabrics were hydroentangled at 0.769 MJ.kg^{-1} specific energy.

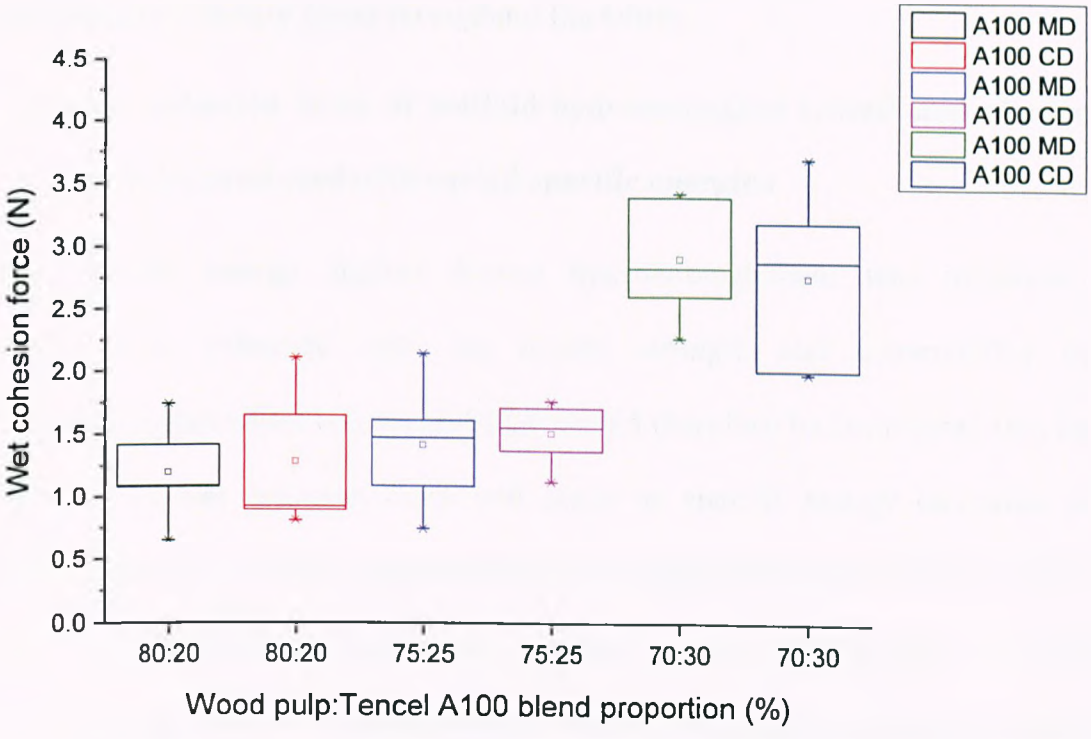


Figure 5.38. Wet cohesion force of wood pulp/Tencel A100 (1.4 dtex, 10mm) wetlaid-hydroentangled fabrics in different blend proportions

Interestingly, no significant difference in MD wet cohesion was observed between fabrics comprised of 20% (1.19N) or 25% (1.42N) Tencel A100 (p = *0.48)*. The wet cohesion values in the MD and CD were found to be very similar. Fabrics comprising 30% Tencel A100 produced higher wet cohesion forces in both MD and CD than the blends composed of 75:25 and 80:20 wood pulp and Tencel A100. The mean MD cohesion force of the fabrics containing 30% Tencel A100 was significantly different than both those containing 20% (p = *0.0003*) and 25% (p = *0.002*). If the forces generated in the shake flask are above the lowest cohesion force (e.g. 0.7 N for 80:20 in the MD direction) the fabric will begin to fragment in the localised area where is it weakest. Fragmentation in

the shake flask works over very small distances and as such the fabrics could be expected to be highly sensitive to the spatial arrangement of pulp and regenerated cellulose fibres throughout the fabric.

5.6.2 Wet cohesion force of wetlaid-hydroentangled lyocell and viscose fabrics produced with varied specific energies

The specific energy applied during hydroentanglement was previously observed to influence both the tensile strength and dispersibility of hydroentangled wipes (section 5.4.2). It would therefore be anticipated that an increase in wet cohesion force will occur as specific energy increases in hydroentangling. In these experiments two regenerated cellulose fibres, with a low and high wet modulus were selected (viscose and standard lyocell, respectively). Wetlaid-hydroentangled fabrics produced composed of 80% wood pulp and 20% of 1.7dtex, 8 mm lyocell or viscose. The specific energy was systematically varied between 0.225 and 0.769 $MJ.kg^{-1}$. The mean wet cohesion force data for both fabrics in the MD and CD at each specific energy are shown in Figure 5.39.

A general increase in the mean wet cohesion force with increasing specific energy was observed. In the fabrics containing lyocell, the mean MD cohesion force obtained at the maximum specific energy that could be applied by the process (0.769 $MJ.kg^{-1}$) was almost four times greater than that achieved at 0.225 $MJ.kg^{-1}$.

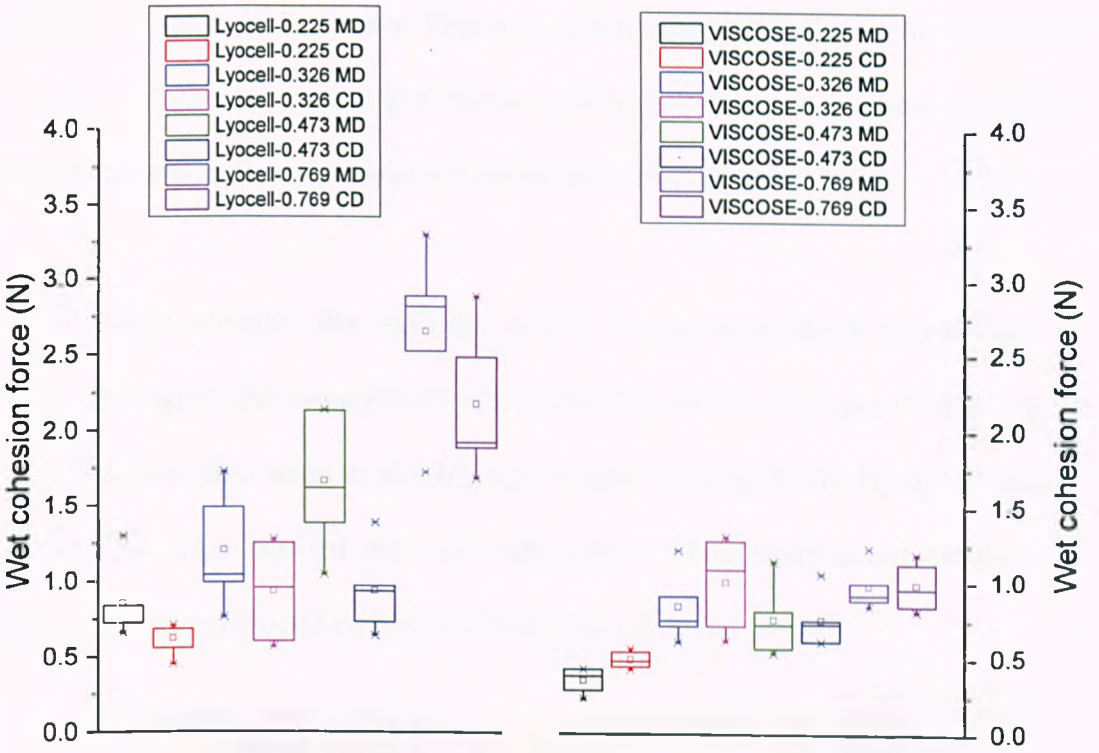


Figure 5.39. Changes in wet cohesion forces with applied specific energy for fabrics composed of 80% wood pulp and 20% lyocell or viscose (1.7dtex, 8 mm)

The corresponding data for the fabrics containing viscose produced only a two times increase as the specific energy increased over the same range. The mean force in the fabrics containing lyocell was therefore more sensitive to increases in specific energy as compared to those containing viscose. This may suggest that fibre entanglement continued to increase in the fabrics containing lyocell over the full range of specific energies, whereas in those containing viscose, no additional fibre entanglement could be introduced at the higher specific energies. This might arise because of the low wet modulus of viscose (Table 2.4), meaning the fibres were fully entangled and rendered incapable of further displacement or entwinement before the higher energies are reached. By contrast, a higher wet modulus fibre such as lyocell requiring more kinetic energy to fully entangle the network will continue to strengthen as the specific

energy continues to increases. This is in addition to the well-known differences in wet tensile strength between viscose and lyocell fibres as shown in Table 2.4, which will also influence the mechanical properties of the fabric.

Interestingly, despite the ease by which viscose-containing fabrics can be hydroentangled, the same fabrics also exhibited excellent dispersibility. Figure 5.40 indicates that even at the highest specific energy 0.769 MJ.kg^{-1}, 100% of the viscose wipe cleared the 3.15 mm screen whilst only about 88% of the fabric containing lyocell cleared the same screen.

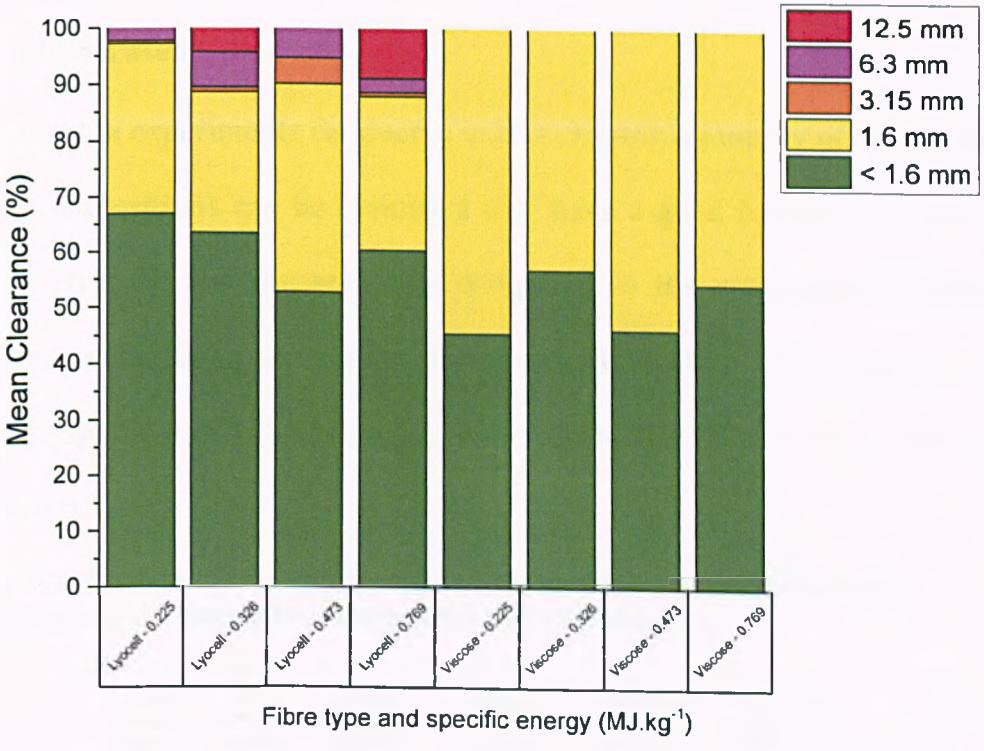


Figure 5.40. Dispersibility of wood pulp-viscose or lyocell (both 1.7dtex, 8 mm) wetlaid-hydroentangled fabrics showing reduced dispersibility with increasing specific energy

These results could suggest that the same fibre properties that enable viscose fibres to entangle so readily at low kinetic energy, particularly the low wet

modulus, could also facilitate disentanglement during agitation even though the kinetic energy due to agitation is not likely to approximate the magnitudes encountered during hydroentangling. Other factors mitigating the dispersion of lyocell could be related to parameters such as fibrillation occurring during shake flask testing, which was observed in the commercial wipes evaluated in chapter 4.7 where fibrils bridging adjacent fibres interfered with their dispersion in to smaller fragments. The role of fibrillation on dispersibility requires further study.

5.7 Identification of high performance experimental wipe substrates

Based on the experiments conducted in this chapter, a number of experimental fabric compositions can be identified that have a good balance of mean wet tensile strength and dispersibility, compared to the commercially-available samples evaluated in section 4.5 and 4.6. Specifications of the experimental wetlaid-hydroentangled fabrics that are of particular interest are summarised in Table 5.1.

Table 5.1. Experimental wetlaid-hydroentangled fabrics with promising combinations of mean MD wet strength and dispersibility

Fibre type	Linear density (dtex)	Fibre length (mm)	Fibre content (%wt)	Pulp content (%wt)	Specific energy ($MJ.kg^{-1}$)	Mean wet breaking load (N/25 mm)	Mean clearance <12.5 mm (%)
Viscose	1.7	10	20	80	0.769	5.26	97.2
A100	1.4	10	20	80	0.769	8.33	95.6
A100	1.4	8	20	80	0.769	5.33	98.9
Lyocell	1.4	6	30	70	0.769	5.66	100

It is evident in Table 5.1 that when standard lyocell is blended with wood pulp to produce a fabric with a high wet strength (>5N/mm) and mean clearance

(above 95% for the <12.5 mm screen), the maximum fibre length than can be used is limited to 6 mm. However, when viscose or Tencel A100 are blended with wood pulp to produce fabrics capable of achieving a high mean clearance value, the fibre length can be increased up to 10 mm. This may be due to the fact that these fibres will have a higher resistance to fibrillation than standard lyocell and will therefore break-up more readily despite the greater mean fibre length. Again, this highlights the potential importance of fibre fibrillation as an area worthy of further study.

In relation to the most promising airlaid-hydroentangled fabrics composed of wood pulp and regenerated cellulose fibres, Table 5.2 indicates that in general, shorter fibre length is required in the regenerated cellulose fibres to achieve an acceptable balance of wet tensile strength and dispersibility compared to the wetlaid-hydroentangled fabrics of similar composition.

Table 5.2. Experimental airlaid-hydroentangled fabrics with promising combinations of mean MD wet strength and dispersibility

Fibre type	Linear density (dtex)	Fibre length (mm)	Fibre content (%wt.)	Pulp content (%wt.)	Specific energy ($MJ.kg^{-1}$)	Mean wet breaking load (N/25mm)	Mean clearance <12.5 mm (%)
A100	1.7	6	30	70	6.85	11.14	100
Lyocell	1.7	6	20	80	6.85	7.25	97.0
A100	1.4	8	30	70	1.192	6.05	100

To compensate for the shorter fibre length in terms of wet strength, it was found possible to increase the proportion of regenerated cellulose fibres in the blend from 20% to 30%. A higher specific energy could also be employed compared to the wetlaid fabrics. Generally, using this strategy, higher mean wet

breaking load values could be achieved, without compromising dispersibility, than was possible with wetlaid-hydroentangled fabrics. Blending the Tencel A100 fibre with wood pulp enabled the highest wet strengths as well as maintaining high levels of dispersibility. Although it is not yet commercially employed in the manufacture of wet wipe substrates, this work highlights the potential for Tencel A100 to be utilised as a blend component in the manufacture of hydroentangled wet wipe substrates. It is also possible to subject this fibre to relatively high specific energy during hydroentangling to generate the necessary frictional resistance required to maintain high wet strength whilst still enabling disentanglement when subjected to testing in the shake-flask, without the risk of fibrillation.

From the data in Table 5.1 and Table 5.2 it may be observed that one wetlaid and one airlaid fabric, both comprised from A100, exceed the aspirational target set in section 2.9 of a threshold wet tensile strength of 15 N/50 mm and ≥95% dispersibility (12.5mm apertured screen) performance, using the shake-flask method of dispersibility testing. An airlaid fabric exceeding 22 N/50 mm with 100% dispersibility has been achieved.

5.8 Empirical modelling for airlaid-hydroentangled fabrics composed of blends of wood pulp and regenerated cellulose fibre

It is evident that there are multiple factors affecting the wet strength and dispersibility of a hydroentangled nonwoven fabric containing wood pulp and short cut regenerated cellulose fibre. No single compositional, dimensional or

process-related factor can fully account for differences in wet strength or dispersibility. To further elucidate the influence of factors, empirical models were evaluated based on multiple regression modelling techniques. This work was carried out using data generated from measurements of airlaid-hydroentangled fabrics produced in this study that were composed of wood pulp and regenerated cellulose fibres. Experimental data from the wetlaid-hydroentangled fabrics of similar construction were not used in the generation of the empirical models due to the limited variation in the process conditions and fibre compositions that was possible because of the use of the commercial pilot line. Using this pilot line, due to its technical configuration, it was not possible to vary process conditions substantially.

Multiple regression analysis is a method for explanation of phenomena and prediction of future events. It is a useful method of building a relationship model with one dependent variable (either dispersibility or wet breaking load) and more than one independent variable, e.g. fibrillation, total fibre length and specific energy. The multiple regression equation takes the form:

$$y = b_1x_1 + b_2x_2 + \ldots\ldots + b_nx_n + c$$

Where, the *b* terms are the regression coefficients, representing the amount the dependent variable y changes when the corresponding independent variable changes by 1 unit. Associated with multiple regression is the value of R^2, the Coefficient of Determination, which is the percentage of variance in the dependent variable explained collectively by all of the independent variables. The airlaid-hydroentangled fabric data were statistically analysed (IBM SPSS

Statistics 22). Two thirds of the data was used to generate the mathematical model then the final third of the data was used to validate the model by comparing experimental values against predicted.

Initially, a scatter matrix was constructed to visualise the data for the experimental airlaid-hydroentangled fabrics evaluated during the course of this study (Figure 5.41). Area density was excluded because it cannot be considered an independent variable and affects the value of the total fibre length. Not surprisingly, given the multiple factors affecting results, few correlated relationships could be discerned between the fabric parameters and either wet tensile strength or dispersibility. However, it was evident that the mean wet breaking load was positively correlated with increasing specific energy and total fibre length but decreased with increasing non-fibrillating fibre content (viscose and Tencel A100) compared to fibres susceptible to fibrillation (lyocell). Fibrillation was treated numerically with 0 being assigned to fibres that fibrillate and 1 being non-fibrillating fibres.

Statistics 22). Two thirds of the data was used to generate the mathematical model then the final third of the data was used to validate the model by comparing experimental values against predicted.

Initially, a scatter matrix was constructed to visualise the data for the experimental airlaid-hydroentangled fabrics evaluated during the course of this study (Figure 5.41). Area density was excluded because it cannot be considered an independent variable and affects the value of the total fibre length. Not surprisingly, given the multiple factors affecting results, few correlated relationships could be discerned between the fabric parameters and either wet tensile strength or dispersibility. However, it was evident that the mean wet breaking load was positively correlated with increasing specific energy and total fibre length but decreased with increasing non-fibrillating fibre content (viscose and Tencel A100) compared to fibres susceptible to fibrillation (lyocell). Fibrillation was treated numerically with 0 being assigned to fibres that fibrillate and 1 being non-fibrillating fibres.

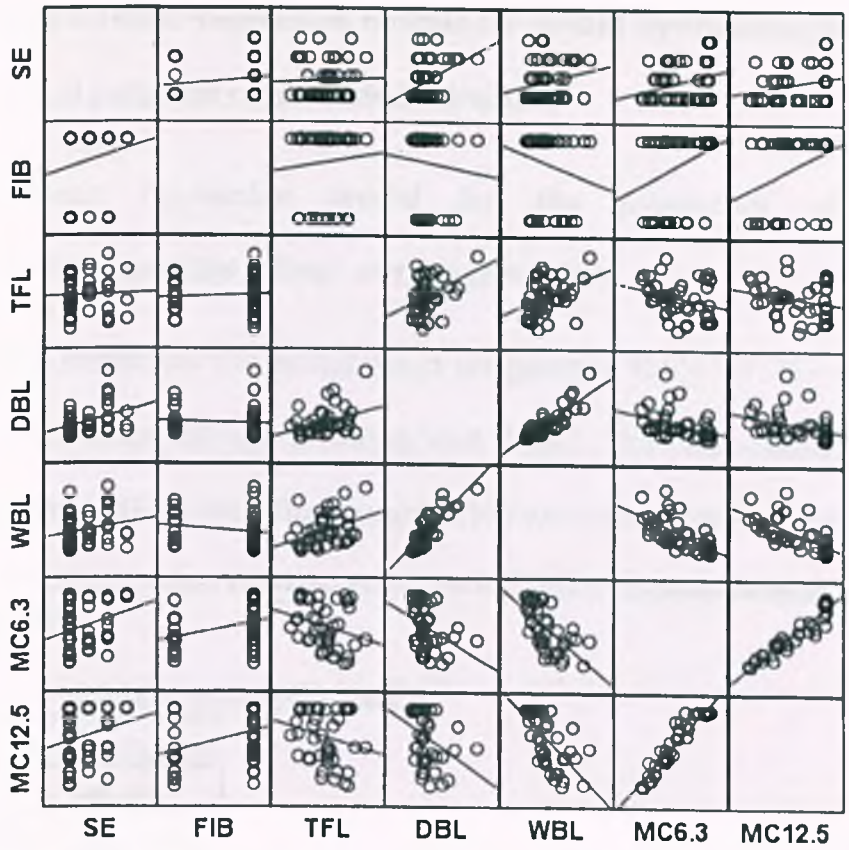


Figure 5.41. Scatter matrix plotting airlaid-hydroentangled fabrics structure and process parameters against mean wet breaking load and mean clearance through a 6.3 and 12.5 mm screen

SE = Specific energy (MJ.kg^{-1}), FIB = fibrillation (0 = fibrillating fibre, 1 = non-fibrillating), TFL = Total fibre length (m), DBL = Mean dry breaking load (N/25mm), WBL = Mean wet breaking load (N/25mm), MC6.3 = Mean Clearance <6.3mm (%), MC12.5 = Mean Clearance <12.5mm (%)

Although they were not strongly correlated, there was an indication of a reduction in dispersibility as the wet tensile strength increased. Dispersibility generally decreased with increasing total fibre length. The incorporation of fibrillation-resistant fibres in the blend, such as viscose and Tencel A100, appeared to improve the dispersibility.

5.8.1 Multiple linear regression models for airlaid-hydroentangled fabrics (wood pulp and regenerated cellulose)

5.8.1.1 Linear regression model for the prediction of airlaid-hydroentangled fabric - wet breaking load

The ANOVA results for the airlaid wipes are given in Table 5.3. The dependant variable was mean MD wet breaking load (WBL). The independent variables were fibrillation (FIB), total fibre length (TFL) and specific energy (SE).

Table 5.3. Multiple linear regression results for airlaid-hydroentangled data - wet breaking load

Variables Entered/Removed[a]

Model	Variables Entered
1	TFL, FIB, SE[b]

a. Dependent Variable: WBL

Model Summary

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	.456[a]	.208	.156	2.56737

a. Predictors: (Constant), TFL, FIB, SE

ANOVA[a]

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	79.395	3	26.465	4.015	.013[b]
	Residual	303.203	46	6.591		
	Total	382.598	49			

a. Dependent Variable: WBL

b. Predictors: (Constant), TFL, FIB, SE

Coefficients[a]

Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.
		B	Std. Error	Beta		
1	(Constant)	.498	1.908		.261	.795
	SE	.468	.214	.304	2.182	.034
	FIB	-1.318	.815	-.214	-1.618	.113
	TFL	3.938E-5	.000	.414	2.976	.005

a. Dependent Variable: WBL

SE = Specific energy (MJ.kg^{-1}), FIB = fibrillation (0 = fibrillating fibre, 1 = non-fibrillating), TFL = Total fibre length (m), WBL = Mean wet breaking load (N/25mm)

From the ANOVA in Table 5.3 F=4.015 on 3 and 46 degrees of freedom gives a p-value of <0.013, meaning the null hypothesis is rejected and at least one of the factors is useful for predicting mean MD wet breaking load. The coefficients table suggests retention of specific energy (*p= 0.034*) and total fibre length (*p = 0.005*) parameters in the model.

Specific energy and total fibre length were inputted as independent variables into the model, with mean wet breaking load as the dependant variable. The results are given in Table 5.4.

From the ANOVA in Table 5.4, F=6.917 on 2 and 44 degrees of freedom gives a p-value of <0.02, meaning the null hypothesis is rejected and at least one of the predictors is useful for predicting mean MD wet breaking load. The coefficients table suggests retention of specific energy and total fibre length parameters in the model.

Table 5.4. Airlaid-hydroentangled forward selection multiple regression output - wet breaking load

Variables Entered/Removed[a]

Model	Variables Entered
1	TFL, SE[b]

a. Dependent Variable: WBL

Model Summary

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	.489[a]	.239	.205	2.56555

a. Predictors: (Constant), TFL, SE

ANOVA[a]

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	91.051	2	45.526	6.917	.002[b]
	Residual	289.610	44	6.582		
	Total	380.661	46			

a. Dependent Variable: WBL

b. Predictors: (Constant), TFL, SE

Coefficients[a]

Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.
		B	Std. Error	Beta		
1	(Constant)	-.687	1.905		-.361	.720
	SE	.908	.313	.390	2.906	.006
	TFL	3.830E-5	.000	.383	2.853	.007

a. Dependent Variable: WBL

The multiple regression equation is given in Equation 5.2:

$$y = 0.908\,x_1 + 3.83E^{-5}x_2 - 0.498$$

Equation 5.2

Where,

y = Mean MD wet breaking load (N/25 mm)

x_1 = Specifc Energy ($MJ.kg^{-1}$)

x_2 = Total fibre length (m)

The removal of fibrillation as a predictor from the regression model is perhaps unsurprising given that the non-fibrillating fibres (Tencel A100) used in the experiments exhibit only 10% lower tenacity compared to fibres susceptible to fibrillation (lyocell) (257). The influence of fibre fibrillation on the wipe's wet strength can be expected to be relatively low since the water pressures utilised during hydroentangling were insufficient to induce intensive primary and secondary fibrillation of constituent fibres.

5.8.1.2 Linear regression model for the prediction of airlaid-hydroentangled fabric dispersibility

The data for the regression model for the airlaid wipe dispersibility is given in Table 5.5. The dependent variable was the mean clearance using the <6.3mm screen. The independent variables were fibrillation, total fibre length and specific energy since each of these parameters was expected to influence the degree of frictional resistance between fibres in the fabric that would need to be overcome as the fabric attempts to disintegrate.

From the ANOVA in Table 5.5 F=6.917 on 3 and 46 degrees of freedom gives a p-value of <0.001, meaning the null hypothesis is rejected and at least one of the predictors is useful for predicting mean wet breaking load. The coefficients table suggests retention of all parameters in the model; Specific Energy ($p = 0.015$), fibrillation ($p = 0.013$) and total fibre length ($p = 0.036$).

Table 5.5. Airlaid-hydroentangled fabric forward selection multiple regression output, prediction of dispersibility

Variables Entered/Removed[a]

Model	Variables Entered
1	TFL, FIB, SE[b]

a. Dependent Variable: MC6.3

Model Summary

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	.581[a]	.337	.294	16.62443

a. Predictors: (Constant), TFL, FIB, SE

ANOVA[a]

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	6463.429	3	2154.476	7.796	.000[b]
	Residual	12713.096	46	276.372		
	Total	19176.526	49			

a. Dependent Variable: MC6.3

b. Predictors: (Constant), TFL, FIB, SE

Coefficients[a]

Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.
		B	Std. Error	Beta		
1	(Constant)	83.770	12.353		6.782	.000
	SE	3.494	1.388	.321	2.517	.015
	FIB	13.646	5.276	.313	2.586	.013
	TFL	-0.0002	.000	-.275	-2.158	.036

a. Dependent Variable: MC6.3

•

SE = Specific energy (MJ.kg^{-1}), FIB = fibrillation, TFL = Total fibre length (m), MC6.3 = Mean Clearance <6.3mm (%)

The multiple regression equation is given in Equation 5.3:

$$y = 3.494\,x_1 + 13.646x_2 + -2.0\times10^{-4}x_3 + 83.77$$

Equation 5.3

y = Mean clearance <6.3mm (%)
x_1 = Specifc Energy (MJ. kg^{-1})
x_2 = Fibrillation (0 = fibrillating fibre, 1 = non fibrillating)
x_3 = Total fibre length (m)

The retention of all predictors in the model suggests that total fibre length, specific energy and the use of non-fibrillating fibres influence the dispersibility performance. The model suggests that total fibre length has a negative influence on dispersibility, i.e. increasing the total fibre length will reduce dispersion. The incorporation of fibres that are resistant to fibrillation is also suggested by the model to benefit dispersion.

5.8.2 Validation of the airlaid-hydroentangled fabric regression models for wet tensile strength and dispersibility

With two thirds of the data used to generate the model the final third of the data was used to validate the model by comparing experimental values against predicted. A plot comparing actual and predicted values for mean MD wet breaking load is shown in Figure 5.42.

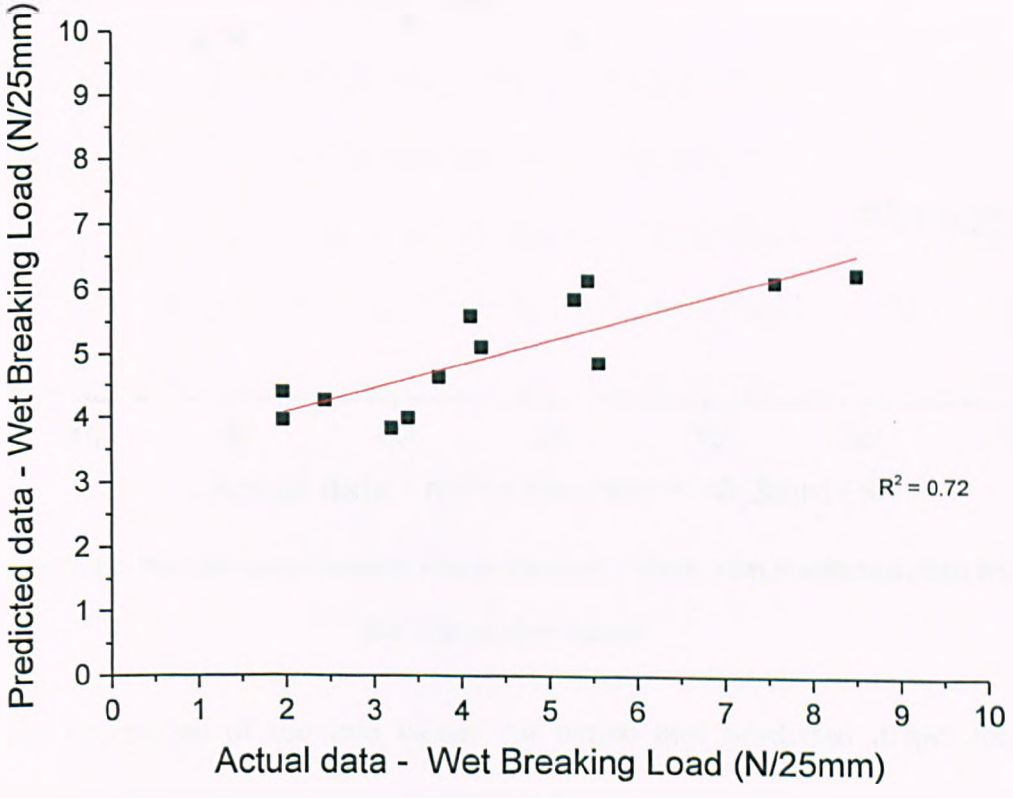


Figure 5.42. Comparison of actual and predicted values from the regression model for mean wet breaking load

Linear regression of the two values for actual and predicted datasets suggests that the multiple regression model is relatively accurate; the coefficient of determination, r^2, is approximately 0.72 for wet MD breaking load.

The model for dispersibility was also validated using the final third of the airlaid-hydroentangled fabric experimental data. The predicted mean clearance and actual mean clearance is plotted in Figure 5.43.

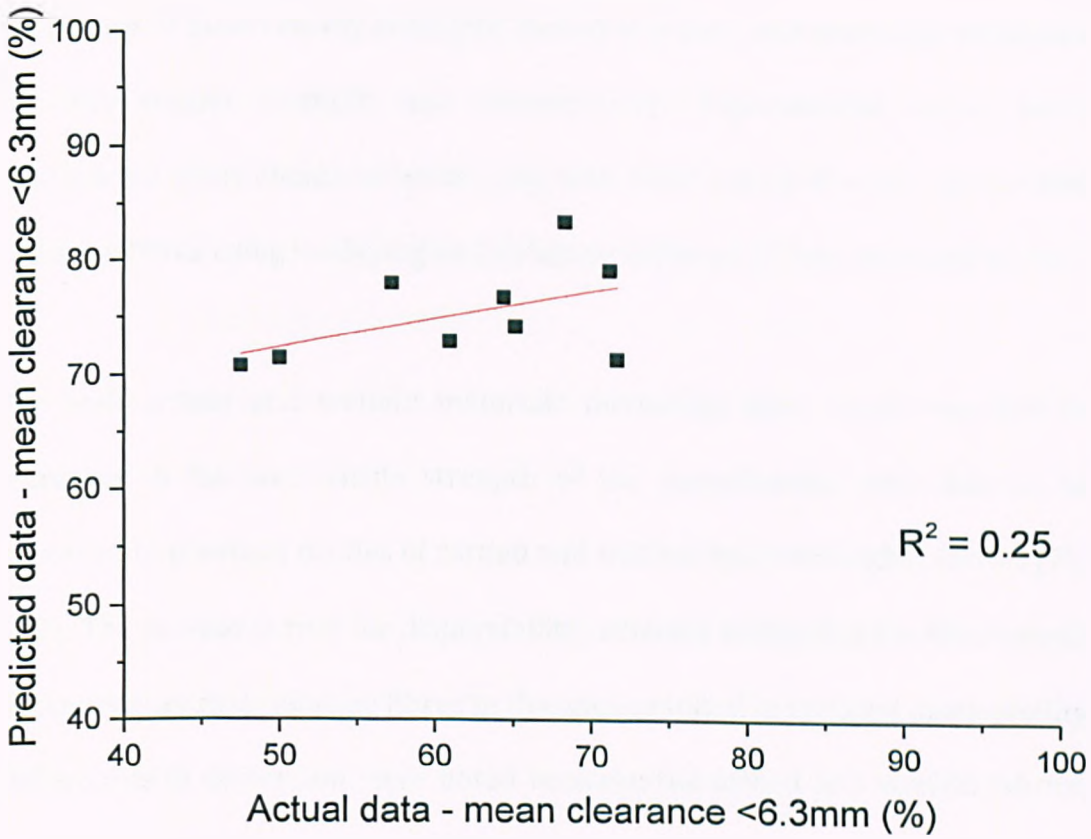


Figure 5.43. Plot of experimental mean clearance data with predicted data from the regression model

Linear regression of the two values for actual and predicted dispersibility suggests that the multiple regression model does not result in good agreement, with a coefficient of determination, r^2=0.25 for mean clearance. This is not surprising because dispersibility cannot easily be represented by a single, unitary value, and is characterised in terms of clearance of various screen sizes. However, there is still benefit in exploring such a model as a relative indicator of how structural parameters might influence the dispersibility.

5.9 Summary

The main aim of this chapter was to understand the influence of composition and process on wipe properties and build knowledge of the factors affecting the properties of mechanically entangled flushable wipes, with particular emphasis on wet tensile strength and dispersibility. Experimental wipes were constructed from blends of wood pulp and short cut (≤10 mm) regenerated cellulose fibres using wetlaying and airlaying followed by hydroentanglement.

For both airlaid and wetlaid materials increasing fibre length resulted in increases in the wet tensile strength of the experimental wipe fabrics, as observed in previous studies of carded and wetlaid hydroentangled fabrics (75, 122). The inverse is true for dispersibility, wherein increasing the fibre length of the regenerated cellulose fibres in the wipe resulted in reduced dispersibility. Differences in dispersion were noted between the airlaid and wetlaid fabrics, with the wetlaid samples exhibiting increased dispersion. This disparity in dispersion performance is highly likely to be a result of the increased specific energies inputted during hydroentanglement for the airlaid fabrics. There was a decrease in dispersibility evident when increasing the fibre length from 8 and 10 mm fibre lengths. However, it was interesting to note that some of the samples containing fibres of 10 mm dispersed well despite the increased fibre length, suggesting there are other parameters that influence dispersibility as well as fibre length, such as the propensity for a fibre to fibrillate and the specific energy employed during hydroentanglement.

The fibre linear density and aspect ratio are considered to be an important influence on wipe wet tensile strength. As the aspect ratio increased the wet tensile strength increased for both airlaid and wetlaid wipes. Unexpectedly, wetlaid wipes' wet tensile strength increases at a faster rate than airlaid suggesting the optimal aspect ratio could be different for each process, i.e. lower for wetlaid-hydroentangled wipes. The reason for this could be related to differences in web density affecting the level of bonding. Dispersibility was found to decrease with increasing aspect ratio, particularly noticeably above 800, which would suggest the upper limit for aspect ratio is lower than the 3000 recommended by Tanio et al (136).

Substituting viscose with highly crystalline cellulose fibres, such as lyocell or Tencel A100 increases the wet tensile properties of hydroentangled wipes. Viscose and Tencel A100 exhibit increased dispersion compared to lyocell. Increasing the proportion of longer fibres increases the number of fibre ends available for entanglement and results in an increase in wet tensile strength. Dispersibility reduces when increasing the proportion of regenerated cellulose in the wipe, although Tencel A100 appears to maintain an acceptable dispersibility performance. Specific fibre blend was also found to influence the wet tensile strength, although not in a linear fashion, both increasing and decreasing the fibres per unit weight resulted in increases in wet tensile properties. This was due to increasing fibre length (decreasing fibres/g) and increasing proportions of fibres (increasing fibres/g). Wet tensile strength can be maximised by increasing both the fibre length and proportion of lyocell.

Interestingly, for some airlaid samples, the wet strength is higher than the dry strength, which was found to result from differences in the mechanism of bonding. Dry tensile failure in wetlaid fabrics due to both fibre and hydrogen bond breakage resulted in low strain-high stress behaviour and brittle fracture. The dry airlaid fabric exhibits stick-slip behaviour before tensile failure, suggesting that the fibres are slipping against each other with some fibre breakage resulting in ductile fracture; the influence of hydrogen bonding is limited. In the wet state, both wetlaid and airlaid fabrics exhibit ductile-type stick-slip behaviour as the hydrogen bonds will not be present therefore entanglement friction is largely responsible for generating tensile stress. When the wet entanglement friction exceeds the combination of dry entanglement friction and fibre strength, fabrics with wet tensile strength higher than dry can be explained.

The specific energy inputted during hydroentanglement was observed to show a positive correlation with both airlaid and wetlaid wet tensile strength. At low specific energies, the relationship is highly linear, at high specific energies higher variation was observed due to fibres being forced apart by the hydroentanglement, creating unusable fabrics. The dispersibility was observed to reduce with increasing specific energy, therefore, this should be carefully selected dependent upon the fibre composition of the web. The carrier screen design was also found to influence tensile strength. Using an open area ≥38.4% resulted in fibre losses and reduced strength, but there was little difference between 31.8-45.6%. Using a very fine screen resulted in inefficient water removal and reduced tensile strength. Unexpectedly, screens with highest open

area result in the lowest dispersibility performance, which does not correlate with the tensile strength. It is possible that removal of short fibre through the more open screens causes localised areas of intensely entangled longer fibres, which do not disentangle easily.

The mechanism by which dispersibility occurs is not currently understood. The mechanism identified using optical and electron microscopy techniques was one where fibres slide across each other, meaning wet fibre-fibre sliding friction could be critical in conferring dispersibility performance. Shorter fibres provide lower levels of entanglement and shorter distances for fibres to slide before disentangling, which explains why shorter fibres disperse more easily. The wet cohesive force was measured using a wet pull out test. The wet cohesive force for lyocell was higher than for Tencel A100 and viscose fibre suggesting that Tencel A100 and viscose should disperse more easily than standard lyocell, which concurs with the experimental results. The wet cohesion force was also found to increase with increasing specific energy and increasing regenerated cellulose fibre content. The results closely follow those observed with the shake-flask dispersibility test suggesting the test could be a simpler, method of assessing dispersion performance. No change in wet tensile strength was observed after saturation in water for extended periods, suggesting dispersibility is not increased due to time within the sewer network.

Empirical models were developed using multiple linear regression methods to help explain how the independent variables (fibrillation, total fibre length and specific energy) can help to explain the resultant wipe properties such as

dispersibility and wet tensile strength (dependent variable). A summary of the effects of the input parameters on wet MD tensile strength and dispersibility are given in Table 5.6.

Table 5.6 Predicted relationships of input parameters on wet MD tensile strength and dispersibility – airlaid-hydroentangled fabrics comprised of wood pulp-and regenerated cellulose

	Wet tensile strength	Dispersibility
Fibrillation		+
Specific energy	+	+
Total fibre length	+	-

The multiple linear regression models predict that specific energy impacts positively on wet tensile properties and dispersibility. This effect on wet tensile strength was demonstrated experimentally in section 5.4.2. The predicted effect of increasing specific energy resulting in reduced dispersibility was not supported by experimental data. As could be expected, the sum of all the regenerated cellulose fibre lengths within the fabric (Total Fibre Length) showed a positive relationship with wet breaking load but a negative impact on dispersibility, greater fibre length leading to greater numbers of cross-over points and increased levels of entanglement. The airlaid models suggest that including fibres that are resistant to fibrillation, such as viscose and Tencel A100 can lead to improvements in dispersibility when tested using the shake-flask test. The model suggests that these non-fibrillating fibres do not impact on the wet tensile strength as this independent variable was removed from the model.

Chapter 6

The Influence of Fibrillation on Dispersibility

6.1 Introduction

Fibrillation can be defined as the splitting of fibres into fibrils or thin filaments and specifically in paper-making the mechanical beating of vegetable fibres is conducted to partially separate fibres in to their component fibrils (140). Fibrillation of cellulosic fibres such as lyocell can have a positive impact on wet tensile strength by increasing the surface area of fibres available for bonding. Several researchers (136, 144, 145) have used this approach to improve wet tensile strength whilst maintaining dispersibility. The wider effects of fibrillation on the dispersibility of wet wipe substrates have not yet been studied in the academic literature. In section 4.7 evidence of fibrillation in commercial wet wipe substrates subjected to shake flask agitation was observed, and this was associated with the regenerated cellulose fibre component rather than the wood pulp. Fibrillation was found to be present in the undispersed residues retained by the screens in the dispersibility test. Recent research by Lang (69) highlighted the potential importance of fibrillation of lyocell and its negative influence on dispersibility. The work was based on a study of fabrics containing high proportions of lyocell (75% by weight), rather than substrates containing no more than 30% by weight, which

is more commonly encountered in a commercial wipe. It remains to be determined if smaller proportions of lyocell in the fabric negatively influence dispersibility as a result of fibre fibrillation. Accordingly, in this chapter the influence of fibre fibrillation on dispersibility was systematically studied using different lyocell fibre grades of varied resistance to fibrillation.

Many cellulosic fibres have the tendency to split into fibrils as a result of their microfibrillar structure (141) provided sufficient mechanical energy is provided. This phenomenon has been exploited in paper making to increase contact area between the fibres resulting in increased dry tensile properties in the final product (142). For many textile applications, uncontrolled fibrillation of fibres is undesirable because it leads to issues with visual appearance, particularly after dyeing (143, 258). Lyocell is susceptible to fibrillation because of its linear, highly crystalline, fibrillar morphology (259). This results in fibres of high wet mechanical strength and a high affinity during dyeing, but there is an inherently low lateral adhesion between the fibril bundles (119). Abrasion in wet conditions can result in substantial fibrillation unless lyocell fabrics are treated or the fibres are chemically modified (258).

Commercially, the most successful method of increasing resistance to fibrillation in lyocell has been crosslinking of the cellulose chains. Since 1998, Tencel A100 has been commercially available, which is cross-linked using TAHT (triacrylamido-trihydrotriazine) (117). TAHT is trifunctional molecule that reacts readily with the hydroxyl groups in cellulose under specific conditions (245). Other low-fibrillating lyocell grades include Tencel LF and

Tencel A300. Although for commercial and regulatory reasons (e.g. formaldehyde content), not all of these low-fibrillating grades of lyocell have been available to the nonwovens industry, it is instructive to understand how greater resistance to fibrillation could influence dispersibility. For this reason, the fibres were made available by Lenzing to enable this study.

6.2 Sample Preparation

Airlaid wipes were constructed using 80% wood pulp and 20% regenerated cellulose fibres. The regenerated cellulose component consisted of 1.4 dtex, 10mm fibres, with the exception of viscose, which was only available in 1.7 dtex. Viscose was also included in the evaluation because it is not normally associated with fibrillation in nonwoven processing or during agitation in the shake flask. The lyocell fibres evaluated were, standard lyocell, Tencel A100 and Tencel A300. Tencel A300 is a cross-linked variant, which is stable in alkaline conditions, originally in order to withstand mercerising conditions in the textile industry. For crosslinking 4,5-Dihydroxy-1,3-dimethyl-2-imidazolidinone is added during fibre manufacture and then cured once in fabric form (knitted or woven) (245). In this study, in cooperation with Lenzing, curing was carried in fibre form to provide a raw material suitable for airlaying. Two variants of Tencel A300 were produced for these experiments, the first designated A300, using the standard concentration of cross-linker and the second designated as A300(2) with double the concentration.

Although fibrillation of lyocell occurs during hydroentangling when high water pressure is employed, the effect can be exploited to modify properties such as

the strength and opacity of the fabric (143, 260, 261). In the present experiment the specific energy used was relatively high (6.85 $MJ.kg^{-1}$) but the water jet pressure did not exceed 50 bar, using the conditions given in Table 3.3.

Scanning Electron Microscopy (SEM) employed after hydroentanglement of the airlaid webs was employed to determine the degree to which fibrillation had occurred, shown in Figure 6.1.

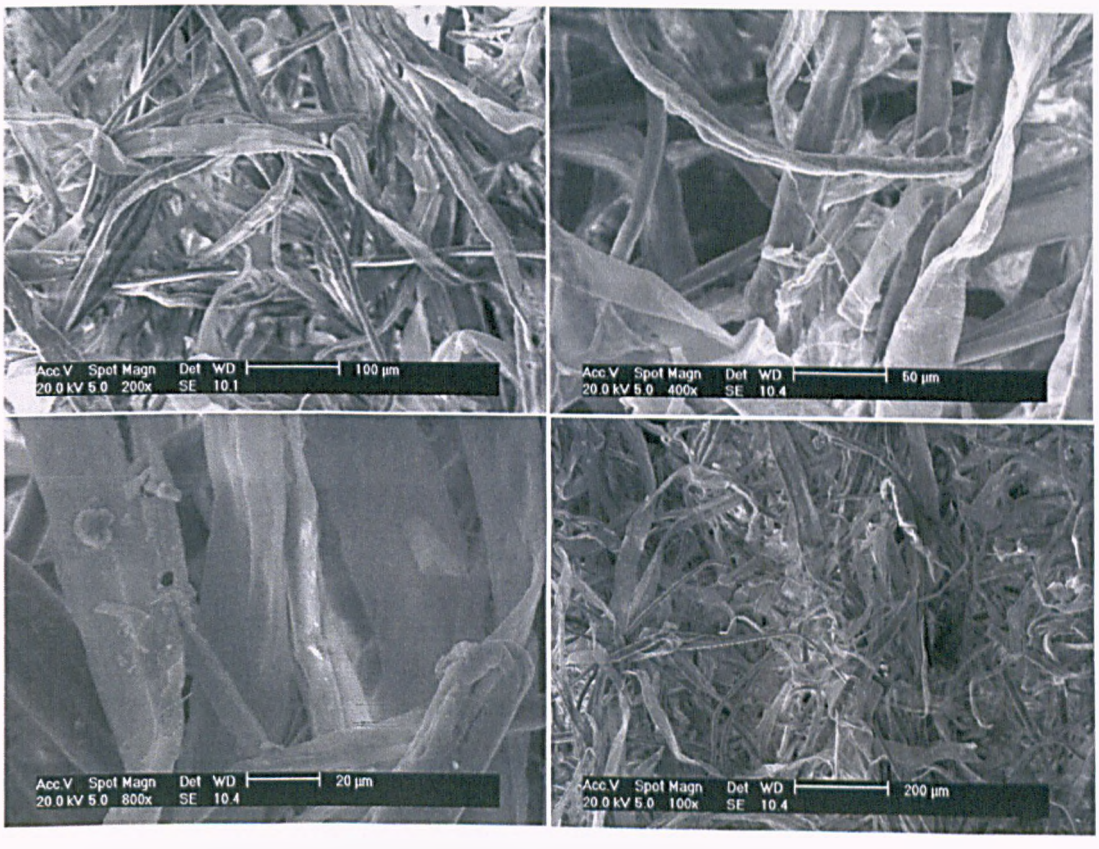


Figure 6.1. SEM micrographs of airlaid-hydroentangled fabric composed of wood pulp and lyocell (1.4 dtex, 10mm) showing little evidence of fibrillation

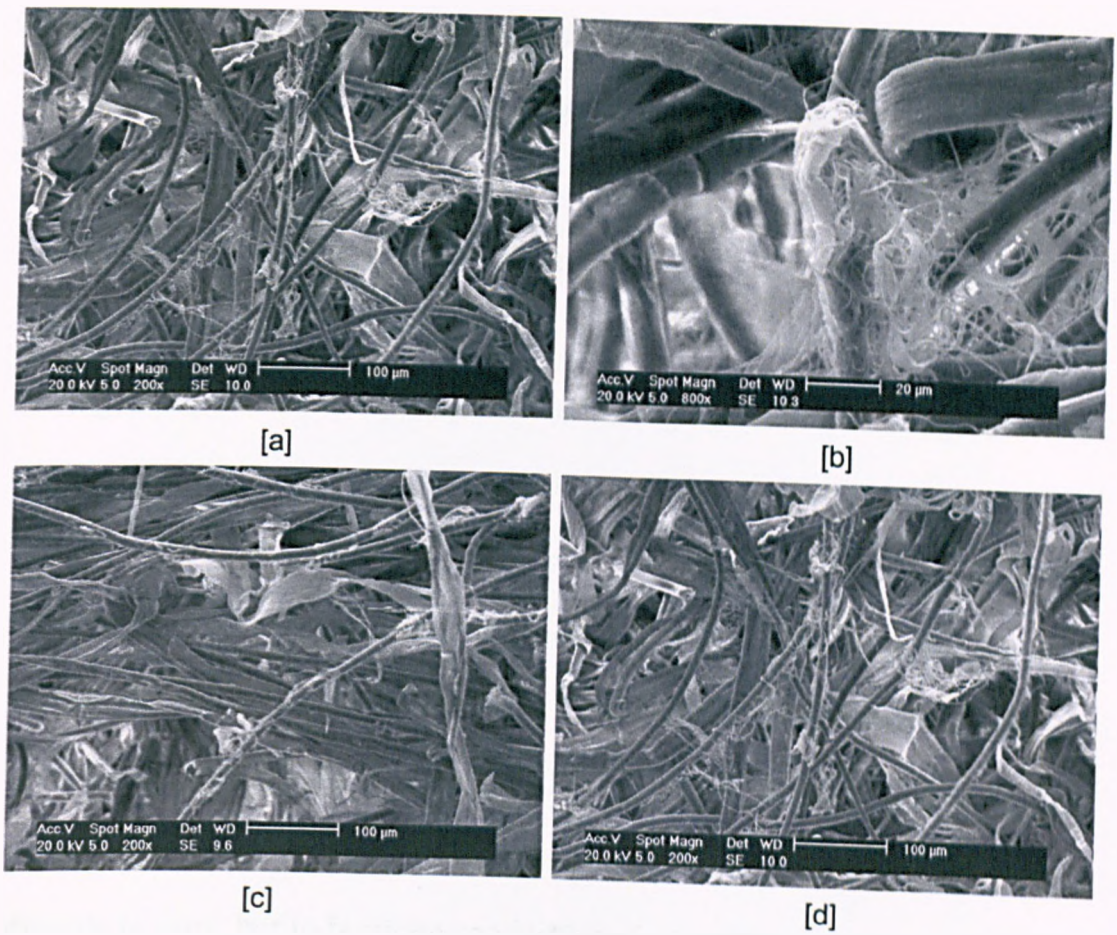
As reflected in Figure 6.1 there was no evidence of fibrillation of the lyocell component. Very limited protrusion of fibrillar material was observed in some individual wood pulp fibres, but this was extremely limited across the whole

sample. A threshold water pressure of 100 bar has previously been suggested as the minimum required to fibrillate lyocell (Tencel) (76) and the peak water pressure used in these experiments was purposely much lower (50 bar) so that any subsequent fibrillation could be isolated to the effect of shake flask agitation during dispersibility testing.

An additional factor influencing the degree to which fibres are able to split is the degree to which they are able to be displaced (261) once the kinetic energy source is applied, since this affects energy transfer. In short-fibre webs the degree to which fibre entanglement and compaction can be developed to prevent fibre movement is more limited than in webs containing much longer fibres, and increasing the water pressure tends to introduce structural irregularities into the web, destroying the structure.

Following hydroentangling, the fabrics were subjected to dispersibility testing using the shake flask method for 6 hr. The fibre residues caught in each screen were carefully collected, air dried in tension-free conditions and studied using SEM. The purpose was to understand the degree to which fibrillation had increased in fibres, compared to the baseline hydroentangled fabric, where virtually no evidence of fibrillation could be detected.

Micrographs of the collected residues after shake flask testing of the airlaid wipe composed of 80:20 woodpulp and standard lyocell (1.4 dtex, 10mm) are shown in Figure 6.2 for each screen. No fibre was captured in the 12.5 mm screen and hence no micrographs for this screen are shown.



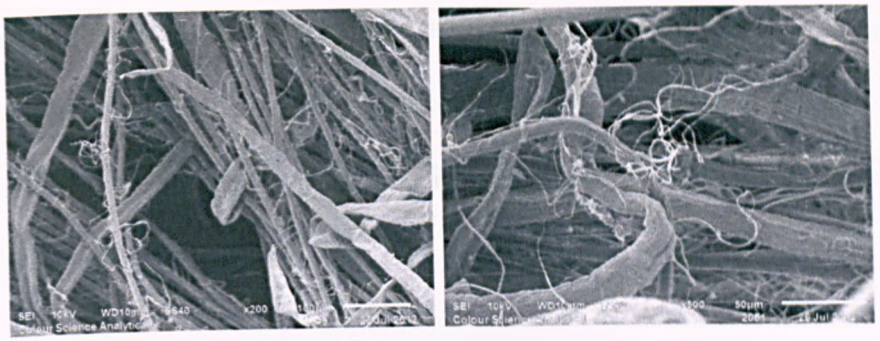
(a) 6.3 mm Screen (b) 6.3mm Screen (c) 3.15mm Screen (d) 1.6mm Screen

Figure 6.2. SEM micrographs of airlaid-hydroentangled wood pulp-lyocell (1.4 dtex, 10mm) wipe after 6 hr dispersibility testing in the shake flask

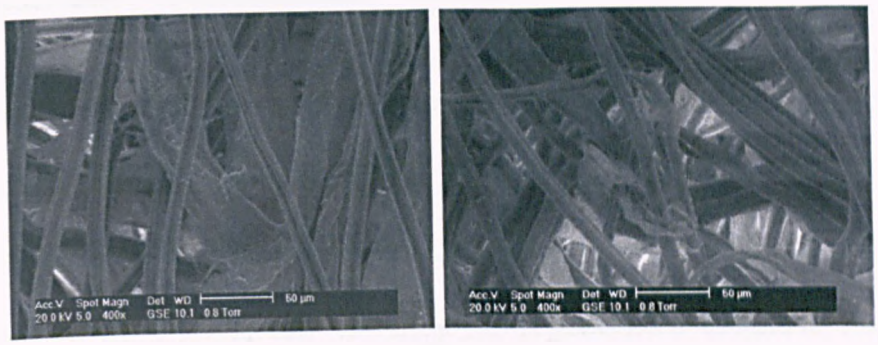
The residual fibre captured in the screens after dispersibility testing clearly exhibited fibrillation associated with the lyocell component. Given that no lyocell fibrillation could be observed in the fabric after hydroentanglement, it was reasonable to assume it had been generated during shake flask agitation. Furthermore, the fibrillation can be considered partly responsible for preventing dispersion and fragmentation of the wipe in dispersibility testing since it was apparent that fibrils were heavily entangled around groups of adjacent fibres preventing their release. The extent of fibrillation was greatest in the residues captured in the largest diameter (6.3 mm) screens, but although

the extent of fibrillation was lower, fibrillated fibre was also present in the residues collected in the smallest screen (1.6 mm).

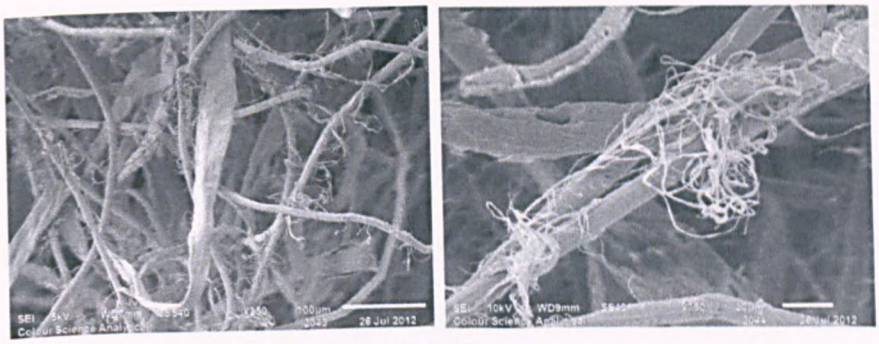
Comparison of the condition of different grades of lyocell fibres (standard lyocell, Tencel A100, Tencel A300) as well as viscose after 6 hr shake flask testing of the fabrics is revealed in the micrographs shown in Figure 6.3. As expected, while there is extensive fibrillation in the fabrics containing standard lyocell, very little fibrillation of the surrounding pulp fibres was observed. Surprisingly, fabrics containing the Tencel A300 fibres also exhibited extensive fibrillation, similar to standard lyocell. This could be indicative of insufficient cross-linking during the production of the samples. Note that the chemical treatment carried out by Lenzing is normally applied to fabric rather than directly to fibre, but to facilitate production of nonwovens, Lenzing treated the material in fibre form especially for the present study. It is possible that the reaction requires further optimisation for fibre production, which is outside the scope of the present work. No fibrillation of viscose was observed after shake-flask test agitation, which was as expected given the structure of the fibre and the low modulus. Usually, as the structure of regenerated cellulose fibres become more fibrillar, and modulus increases, fibrillation would be anticipated. For example, high modulus polynosic viscose fibrillates readily (143). It has been reported that the order of fibrillation resistance of cellulosic fibres (low to high) is Viscose/Modal → Cotton → Polynosic viscose → Standard lyocell (119).



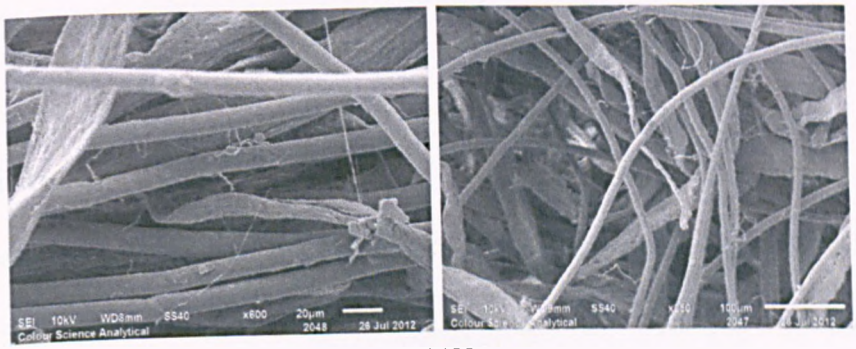
[a] Lyocell



[b] Viscose



[c] A300



[d] A100

Figure 6.3. Micrographs showing fibrillation of standard lyocell, Tencel A100, Tencel A300 and viscose residue after 6hr agitation in the shake flask

In the present experiment, fabrics containing Tencel A100 exhibited very low levels of fibrillation after agitation in the shake flask. Although there was some

evidence of fibrillation in the screen residues, the extent was sufficiently low as to prevent entanglement with adjacent fibres. Consequently, substituting Tencel A100 for standard lyocell would be expected to result in fabrics with much improved dispersibility.

6.3 Resistance to fibrillation

From the SEM analysis of residues collected in the screens, it was observed that regenerated cellulose fibres, including the different variants of lyocell, exhibit markedly different fibrillation resistance. In an effort to quantify the relative resistance to fibrillation, the 'freeness' of regenerated cellulose fibres was measured using the Canadian Standard Freeness (CSF) method described in Section 3.3.3. This method has been employed by previous researchers to assess fibrillation resistance of regenerated cellulose fibres (245). The fibres tested herein were all 1.4 dtex, 10 mm including standard lyocell, Tencel A100, Tencel A300 and Tencel A300(2), detailed in Table 3.1. The viscose fibre was only available in 1.7 dtex, 10 mm.

The CSF test is designed to give a measure of the rate at which a dilute suspension of pulp (3 g of pulp in 1 L of water) may be drained of water. The higher the weight of retained water the lower the 'freeness' of the pulp. A reduction in CSF is observed if the fibre fibrillates (245). The CSF results for each of the short cut fibres studied herein after a fixed period of beating are shown in Figure 6.4.

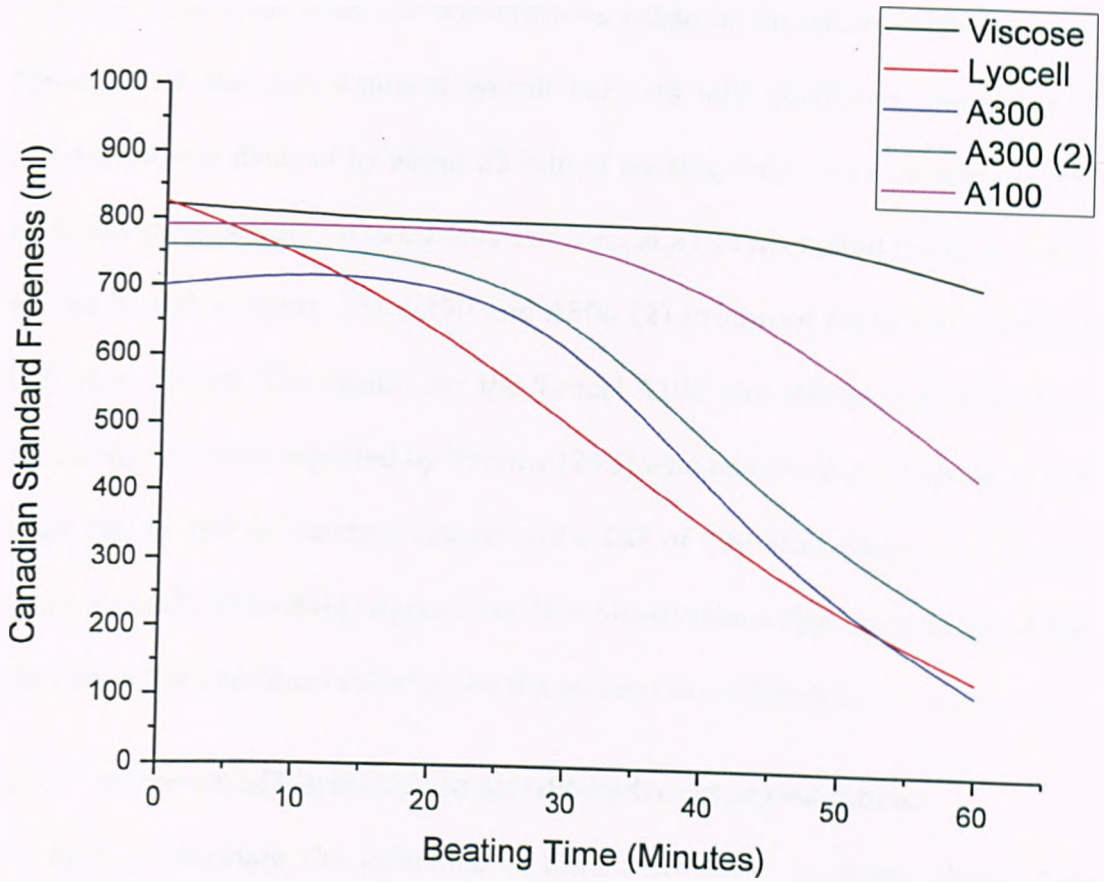


Figure 6.4. Canadian Standard Freeness values for short cut regenerated cellulose fibres (standard lyocell, Tencel A100, Tencel A300, Tencel A300(2) and viscose)

As observed during the SEM investigation, the results in Figure 6.4 suggest that viscose fibres have the highest fibrillation resistance. This is in agreement with the results of Rohrer et al (119) who found that viscose and modal fibres produce the highest fibrillation resistance amongst regenerated cellulosics. The CSF of the standard lyocell decreased linearly with beating time and the CSF value reduced to below 200 ml, which is indicative of poor fibrillation resistance.

All the modified lyocell short cut fibre variants, (Tencel A100, Tencel A300 and Tencel A300(2)) exhibited higher CSF values and greater fibrillation resistance,

which is consistent with the observations made of the shake flask residues. Although all the non-standard lyocell variants still fibrillated, the onset of fibrillation was delayed by about 25 min of beating time. After 25 min the CSF dropped quite rapidly up to 60 min. The Tencel A100 fibrillated the least out of all the lyocell variants. The A300 and A300 (2) produced rapid reductions in CSF after 25 min. The results for the Tencel A100 and standard lyocell fibres are similar to those reported by Burrow (245) who observed a reduction in CSF from 700 to 200 in standard lyocell and a CSF of 700 after 36 min for Tencel A100. Overall, these data support the SEM observations that were made of the fibrillated fibre residues collected by the screens in section 6.2.

6.3.1 Influence of fibrillation in airlaid-hydroentangled fabrics

To further elucidate the influence of fibre fibrillation on dispersibility, the dispersibility of airlaid-hydroentangled fabrics containing cross-linked lyocell fibres, rather than standard lyocell is compared in Figure 6.5. Lyocell, which has known susceptibility to fibrillation, and viscose, which is known to resist fibrillation are also included as negative and positive control samples. The figures include data for a variety of experimental fabrics produced in this study, covering a range of different fibre lengths (8-10 mm), linear densities (1.4 – 1.7 dtex), blend compositions (20% regenerated cellulose content with wood pulp) and processing conditions (specific energies from 0.72-1.192 $MJ.kg^{-1}$). Details of the fibre composition and specific energies used to produce the samples are given in Table 6.1.

Table 6.1. Fibre composition and specific energies used to produce airlaid-hydroentangled fabrics

Fibre Type	Linear Density (dtex)	Fibre Length (mm)	Specic Energy ($MJ.kg^{-1}$)
A100	1.4	8	0.716, 0.954, 1.192
A100	1.4	10	0.716, 1.192
A300	1.4	8	0.716
A300	1.4	10	0.716, 0.954
A300 (2)	1.4	8	0.716, 0.954
A300 (2)	1.4	10	0.716, 0.954
Lyocell	1.4	8	0.716
Lyocell	1.4	10	0.716, 0.954, 1.192
Viscose	1.7	8	0.716
Viscose	1.7	10	0.716, 1.192

A one-way Anova analysis indicated a significant difference between the means at the 0.05 level. The dispersibility of the sample containing the Tencel A100 fibre as a blend component (mean clearance <12.5 mm= 88.33%) was significantly higher than that containing Tencel A300 and standard lyocell (mean clearance <12.5mm 60-70% respectively). Fabrics containing viscose also exhibited excellent dispersibility. Thus, it was apparent that the highest levels of dispersibility were only produced in those fabrics containing a short cut regenerated fibre known to be resistant to fibrillation, such as Tencel A100 or viscose.

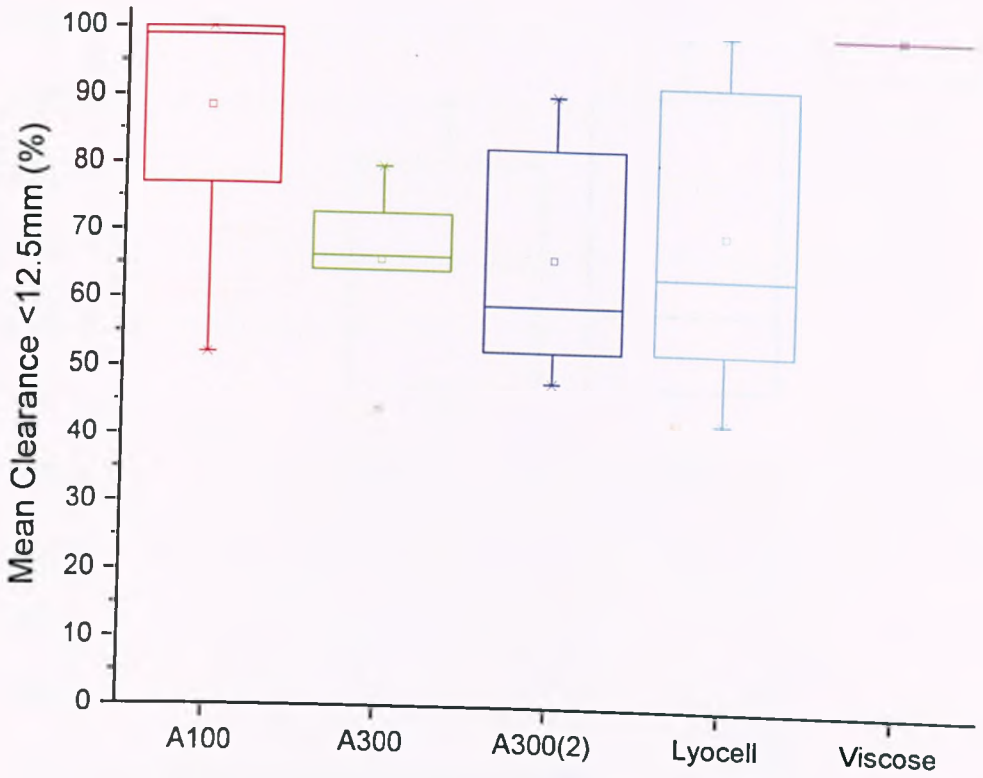


Figure 6.5 Dispersibility of airlaid-hydroentangled fabrics of varying compositions and processing conditions

Fabrics produced with identical specific energies (0.72 $MJ.kg^{-1}$) during production were then compared. These fabrics were composed of 80% wood pulp and 20% regenerated cellulose fibres of 1.4 dtex linear density. Fibre lengths were either 8 mm or 10 mm. As shown in Figure 6.6 at fixed specific energy the effect of incorporating Tencel A100 is more pronounced, with the highest dispersibility amongst the lyocell variants. A two-sample t-test confirmed a significant difference in the values obtained for fabrics containing Tencel A100 and standard lyocell ($p = 0.023$). Fabrics containing Tencel A300 and Tencel A300(2) dispersed poorly in comparison, which can be attributed to higher fibrillating propensity during shake flask agitation.

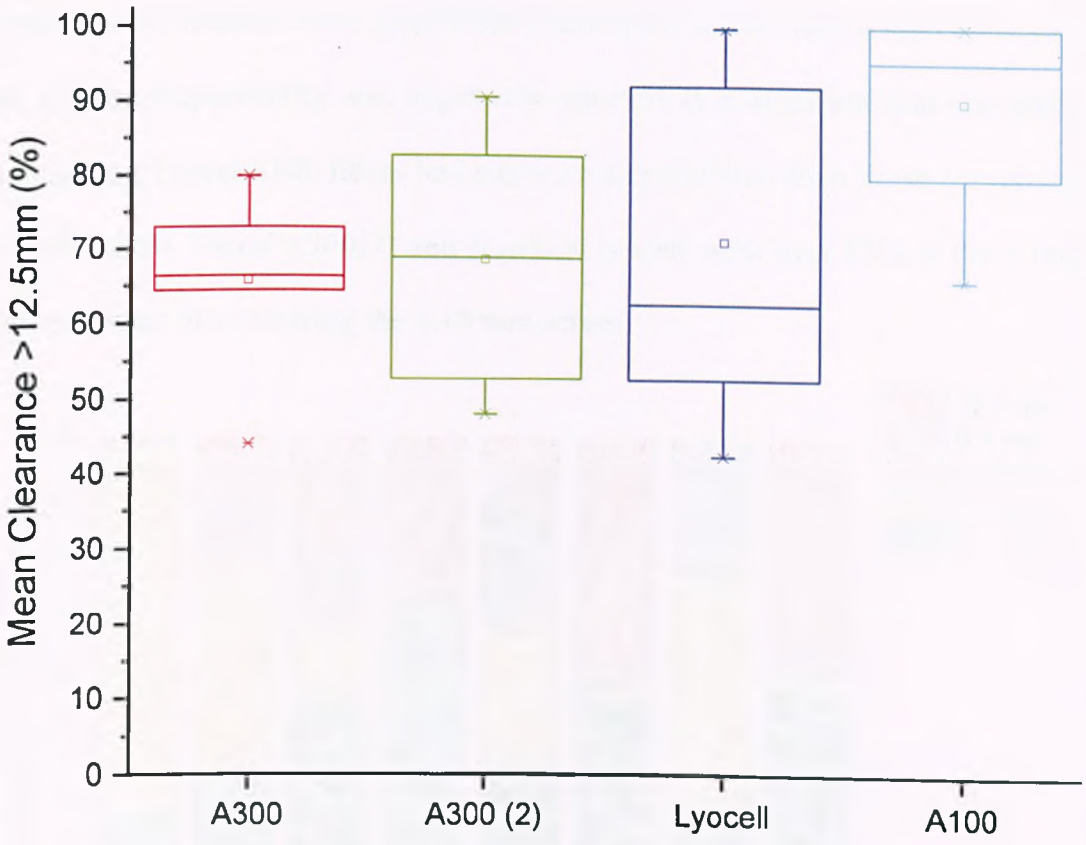


Figure 6.6. Comparison of airlaid-hydroentangled wood pulp-regenerated cellulose fabric dispersibility, specific energy 0.72 MJ.kg^{-1}

Evidence from both the SEM analysis of the shake flask residues, the CSF and the dispersibility tests strongly suggest that the fibrillation resistance of Tencel A100 fibres is sufficient to withstand the 6 hr agitation time associated with shake-flask testing. Practically, the fibrillation resistance of Tencel A300 will need to be improved if the fibre is to be suitable for application in wet wipe substrates.

The dispersibility of airlaid-hydroentangled fabrics containing wood pulp and lyocell is shown in Figure 6.7. The fabrics were all made from 20% 1.4 dtex (8 or 10 mm) regenerated cellulose fibres and 80% wood pulp, at specific energy of 0.72 MJ.kg^{-1} during hydroentanglement. The highest dispersibility was

observed for fabrics constructed from 8 mm fibre. As the fibre length increased to 10 mm dispersibility was negatively affected. It is apparent that the fabric containing Tencel A100 fibres had superior dispersibility than those containing Tencel A300, Tencel A300(2) and standard lyocell, with over 95% of the 8 mm Tencel A100 fibre clearing the 3.15 mm screen.

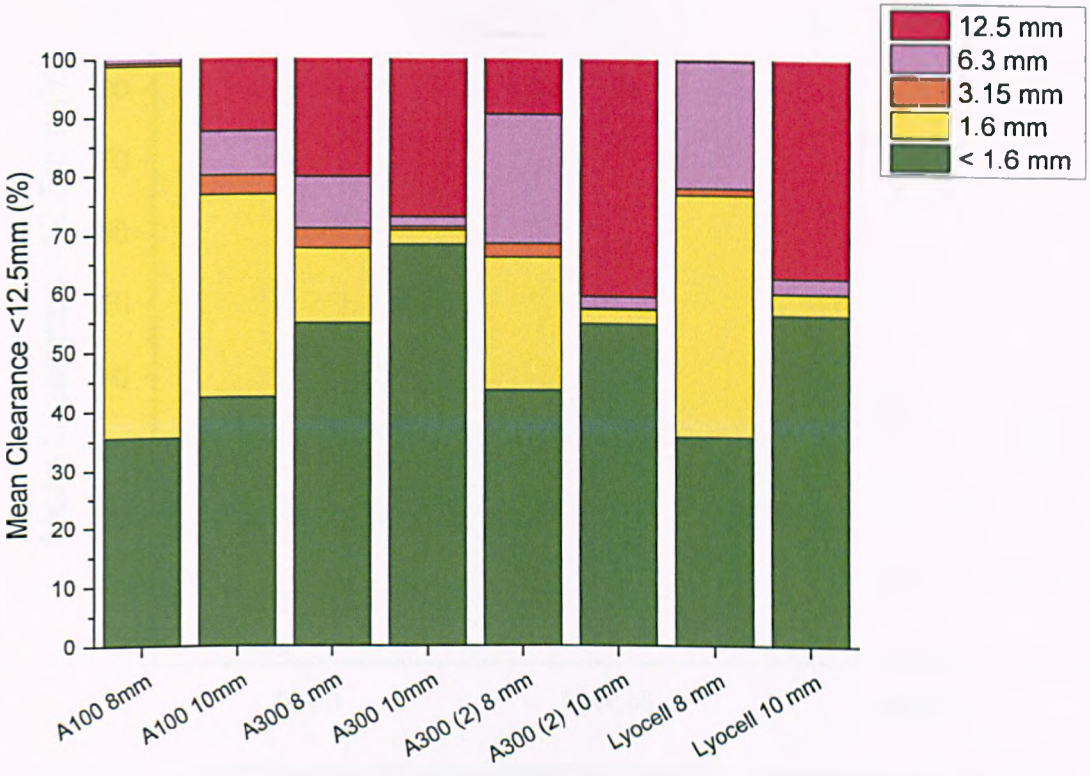


Figure 6.7 Dispersibility of airlaid-hydroentangled wood pulp-regenerated cellulose fabric dispersibility, specific energy 0.72 MJ.kg^{-1}

The poor dispersibility performance of airlaid-hydroentangled fabrics containing Tencel A300 and Tencel A300(2) can be attributed to their fibrillating propensity.

6.3.2 Dispersibility of wetlaid-hydroentangled fabrics

The statistical models discussed in Chapter 5 suggested that the effects of using fibrillation-resistant fibres could offer increases in dispersibility in airlaid

hydroentangled fabrics. To understand if this effect is observed in wetlaid fabrics, the dispersibility of wetlaid-hydroentangled wood pulp fabrics incorporating Tencel A100, standard lyocell and viscose are compared in Figure 6.8.

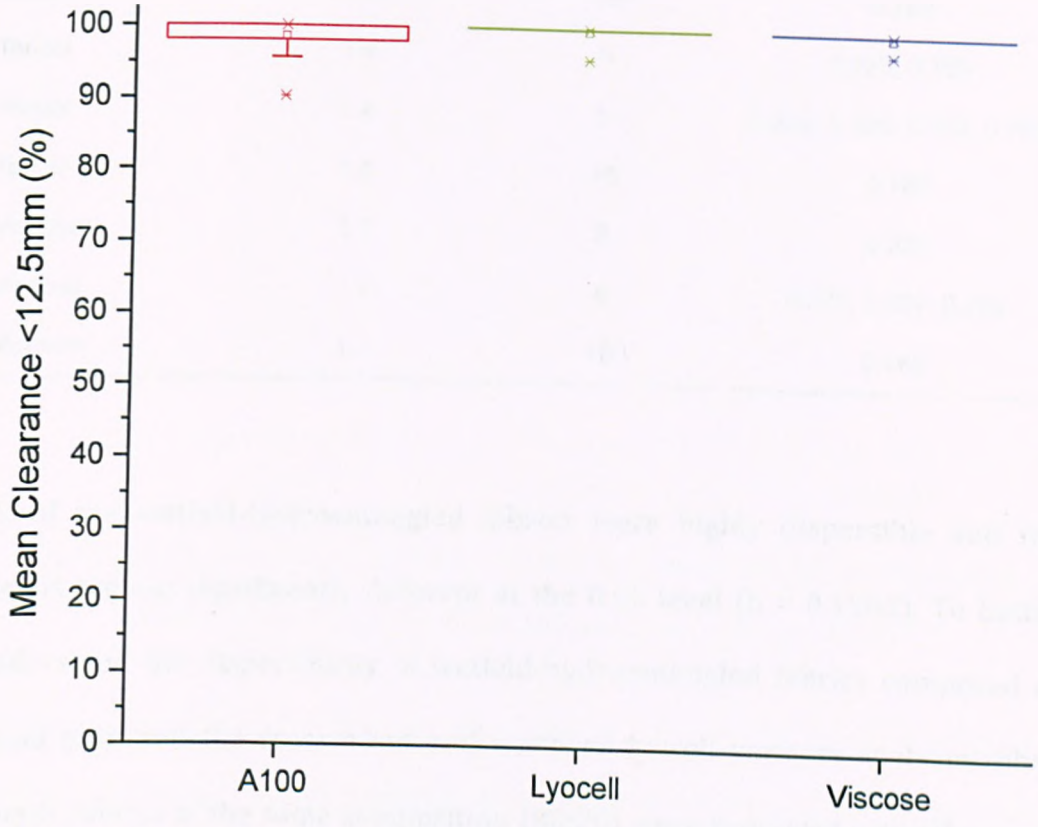


Figure 6.8 Dispersibility of wetlaid-hydroentangled wood pulp-regenerated cellulose fabric dispersibility produced with varying composition and processing

The data includes wetlaid-hydroentangled fabrics composed of 80% wood pulp and 20% regenerated cellulose fibres in which there were variations in fibre length (6-10 mm), linear density (1.4-1.7 dtex) and processing conditions (specific energy: 0.225 – 0.769 $MJ.kg^{-1}$). Details of the fibre composition and specific energies used to produce the samples are given in Table 6.2.

Table 6.2. Fibre composition and specific energies used to produce wetlaid-hydroentangled fabrics

Fibre Type	Linear Density (dtex)	Fibre Length (mm)	Specic Energy ($MJ.kg^{-1}$)
A100	1.4	8	0.769
A100	1.4	10	0.769
Tencel	1.4	6	0.225, 0.769
Tencel	1.4	8	0.225, 0.326, 0.473, 0.769
Tencel	1.4	10	0.769
Viscose	1.7	6	0.225
Viscose	1.7	8	0.225, 0.407, 0.769
Viscose	1.7	10	0.769

All of the wetlaid-hydroentangled fabrics were highly dispersible and the means are not significantly different at the 0.05 level ($p = 0.1582$). To better understand the dispersibility of wetlaid-hydroentangled fabrics composed of wood pulp and the crosslinked and standard lyocell variants at 8 mm fibre length, fabrics of the same composition (80:20) were produced using the same specific energy (0.769 $MJ.kg^{-1}$) and then compared in Figure 6.9.

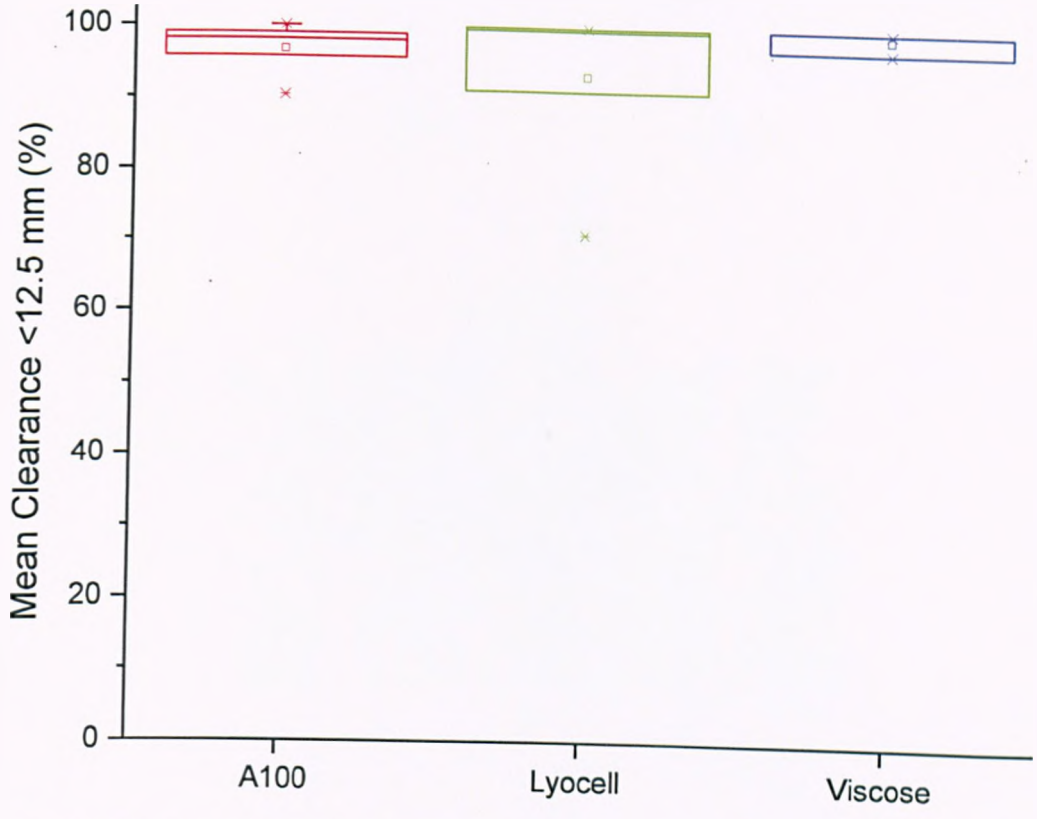


Figure 6.9 Comparison of wetlaid-hydroentangled wood pulp-regenerated cellulose fabric dispersibility, specific energy 0.769 MJ.kg^{-1}

Again, the mean values were not significantly different at the 0.05 level ($p = 0.544$). All of the wetlaid-hydroentangled fabrics exhibited good dispersibility regardless of the regenerated fibre composition in the fabric. So far, the dispersibility in relation to the largest screen (12.5 mm) has been considered, but when the full dispersibility profile of the same fabrics are considered, some interesting patterns emerge (Figure 6.10).

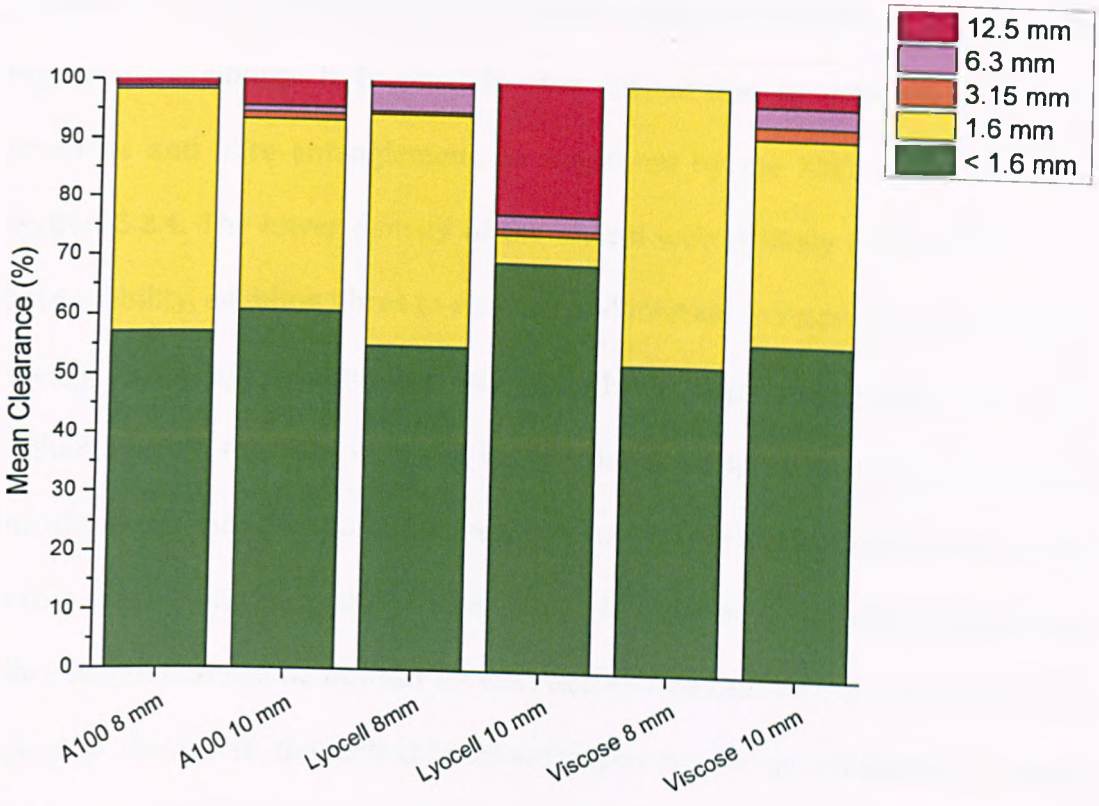


Figure 6.10 Dispersibility of wetlaid-hydroentangled wood pulp-regenerated ceullose fabric, specific energy 0.769 MJ.kg^{-1}

Fabrics composed of non-fibrillating fibres, such as Tencel A100 and viscose, exhibited excellent dispersibility in the smallest screens (1.6 mm and <1.6mm) compared to standard lyocell. All fabrics containing regenerated cellulose fibres constructed from 8 mm fibres dispersed effectively. The benefit of incorporating non-fibrillating fibres is particularly evident when the wetlaid-hydroentangled fabrics contain the longer, 10 mm fibre. Satisfactory dispersibility could not be achieved with standard lyocell using fibres of this length. Therefore, the degree to which the associated wet tensile strength can be increased without compromising dispersibility depends on the use of a non-fibrillating variant of lyocell.

Compared to the airlaid fabrics, the wetlaid substrates exhibited substantially higher dispersibility. It is possible that this is due to differences in web structure and fibre entanglement, as suggested by the XMT observations in section 5.2.4. The lower density of the airlaid web is likely to permit greater fibre mobility, enabling fibres to entwine and migrate in response to the kinetic energy during hydroentangling. During hydroentangling of wetlaid webs, the higher density, together with the highly planar structure is likely to restrict entwinement and rotation of fibre ends, reducing overall fibre entanglement. In terms of achieving acceptable dispersibility, it is also evident that the maximum fibre length that can be utilised for the regenerated cellulose component in the blend is shorter in the airlaid-hydroentangled fabrics as compared to those based on wetlaying. The airlaid-hydroentangled fabrics composed of 10 mm fibres did not disperse well compared to 8 mm and below. In the wetlaid-hydroentangled fabrics, fibre length could be increased to 10 mm fibres whilst still maintaining excellent dispersibility, particularly using non-fibrillating fibres.

For both the airlaid and wetlaid fabrics, when dispersibility is relatively poor and a large proportion of the fibre is captured on the largest screen (12.5 mm), it is interesting to note that the mean clearance of all the screens (<1.6 mm) increases. It is probable that this is due to a greater amount of the wood pulp being released from the structure.

6.4 Influence of fibrillating fibres on wet tensile strength

In addition to dispersibility, the wet tensile strength is of critical importance to ensure adequate function of the wipe. Whilst the use of non-fibrillating fibres as a component in the blend has been found to be helpful in improving dispersibility, the corresponding impact on the fabric's wet strength is unknown. Accordingly, the wet tensile strength of airlaid-hydroentangled fabrics containing wood pulp and non-fibrillating fibres was explored.

6.4.1 Tensile strength of airlaid fabrics constructed from non-fibrillating fibres

All the data for airlaid-hydroentangled fabrics was used to construct a boxplot to compare the general influence of non-fibrillating fibres on tensile strength. A boxplot comparing dry MD tensile strength is shown in Figure 6.11. These data include airlaid fabrics in which the regenerated cellulose fibre component varied in terms of fibre length (6-10 mm), linear density (1.4-1.7 dtex) and process conditions (specific energy). Details of the fibre composition and specific energies used to produce the samples are given in Table 6.3.

Table 6.3. Fibre composition and specific energies used to produce airlaid-hydroentangled fabrics for tensile testing

Fibre Type	Linear Density (dtex)	Fibre Length (mm)	Specic Energy ($MJ.kg^{-1}$)
A100	1.4	6	6.85
A100	1.4	8	0.716, 0.954, 1.192, 1.431
A100	1.4	10	0.716, 0.954, 1.192
A300	1.4	8	0.716
A300	1.4	10	0.716, 0.954
A300(2)	1.4	8	0.716
A300(2)	1.4	10	0.716, 0.954
Lyocell	1.7	6	6.85
Lyocell	1.4, 1.7	8	0.716
Lyocell	1.4	10	0.716, 1.192

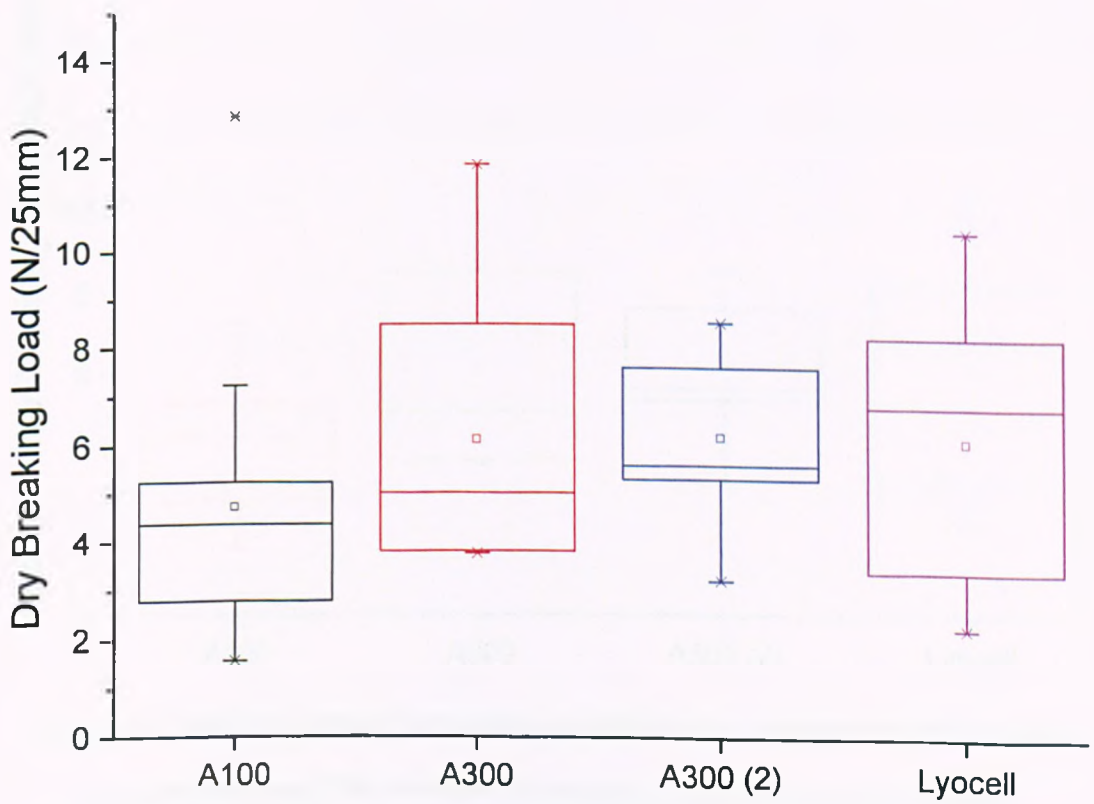


Figure 6.11 Dry MD tensile strength of airlaid-hydroentangled wood pulp-regenerated fibre fabrics of varying composition and specific energies

Comparing the dry tensile strengths of the fabrics containing a proportion of lyocell (standard lyocell, Tencel A100, Tencel A300 and Tencel A300(2)), although values were similar, the A100 Tencel variants tended to produce the lowest values. This could reflect greater bending stiffness and modulus, reducing the degree of entanglement that can be generated during hydroentangling over the same range of specific energies as well as differences in fibre modulus. The corresponding MD wet tensile strength data of the airlaid fabrics is shown in Figure 6.12 and a similar trend was observed as for the dry tensile strength of these fabrics.

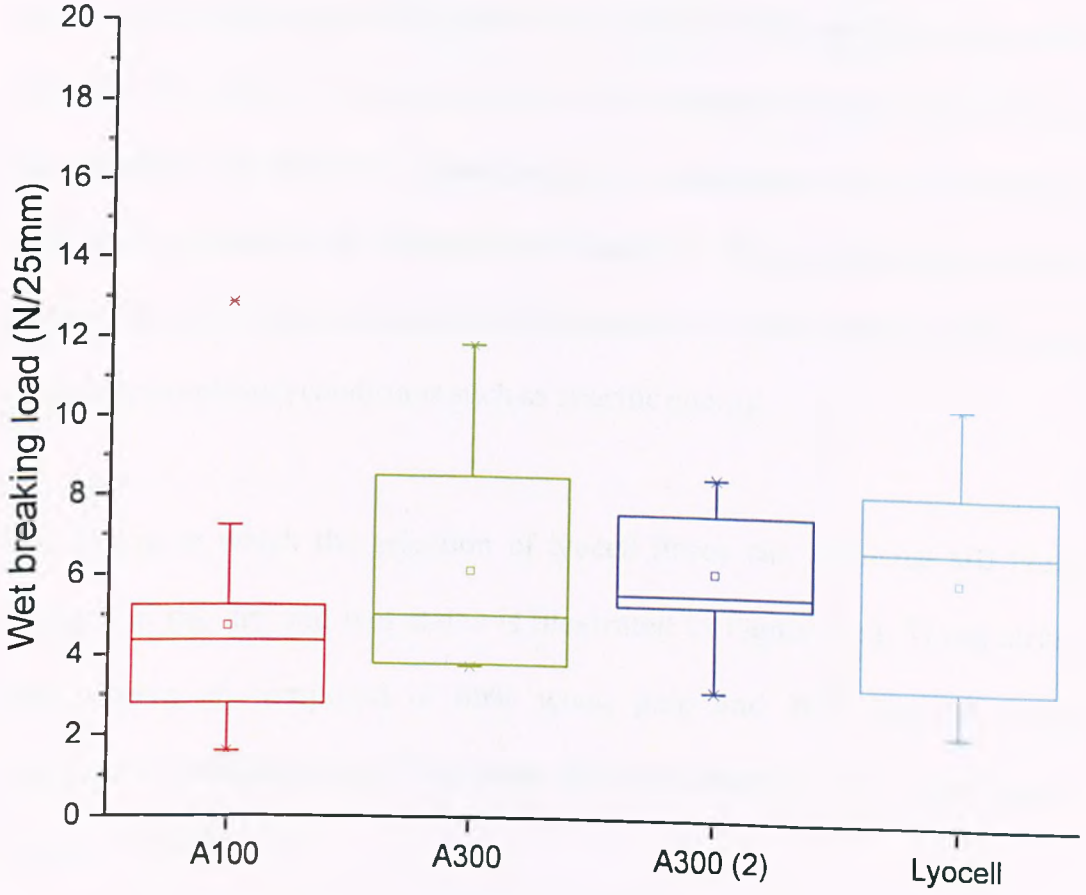


Figure 6.12 Wet MD tensile properties of airlaid-hydroentangled fabrics wood pulp-regenerated fibre fabrics of varying composition and processing

Again, the fabric containing the Tencel A100 fibre produced fabrics with the lowest wet tensile strength. It was discovered in section 5.6.1, that the wet

cohesion (pull-out) force between Tencel A100 fibres is lower than with standard lyocell, which can be expected to be reflected in overall tensile strength. Additionally, the tenacity of Tencel A100 fibre is known to be approximately 10% lower than standard lyocell (257).

Carded-hydroentangled fabrics produced from much longer regenerated cellulose fibres are known to reduce in strength when wet (75). Surprisingly, in the airlaid-hydroentangled samples, the fabrics containing lyocell maintained a similar strength when wet as dry, or in cases the wet tensile strength was higher in the wet state (wet:dry tensile ratio 1.0-1.3). This trend was repeatedly observed, but only for the airlaid fabrics. The behaviour suggests that fibre to fibre friction, wet frictional properties and entanglement levels do influence final fabric properties as discussed in Chapter 5. These parameters will be affected by the mechanical and physical properties of the constituent fibres, as well as by processing conditions such as specific energy.

The degree to which the selection of lyocell fibres can influence MD fabric strength in the dry and wet states is illustrated in Figure 6.13. These airlaid fabrics were all composed of 80% wood pulp and 20% 8mm, 1.4 dtex regenerated cellulose fibre. They were hydroentangled at the same specific energy (0.72 $MJ.kg^{-1}$).

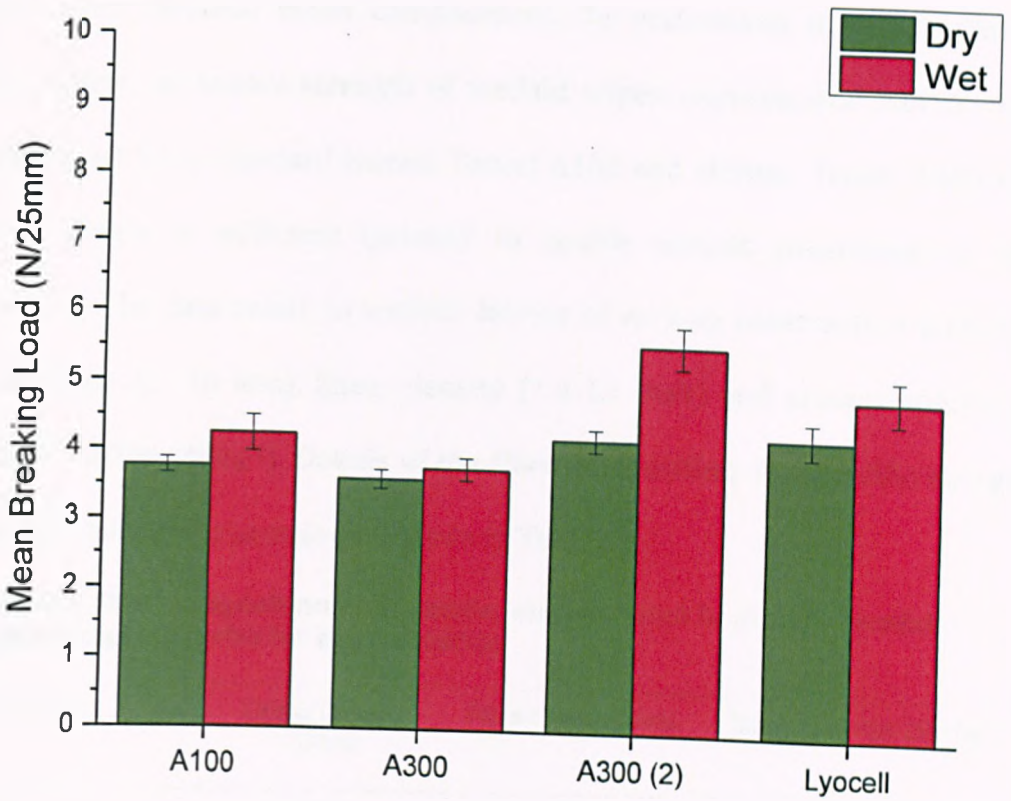


Figure 6.13 Wet and dry MD tensile properties of airlaid-hydroentangled fabrics composed of wood pulp and lyocell fibres (8mm, 1.4 dtex)

In these fabrics, the wet strength was found to be similar or slightly higher than the dry strength, which was quite unexpected. The underlying explanation for this behaviour was discussed in section 5.3.2. The fabrics containing Tencel A300 (2) produced the highest wet to dry strength ratio (1:1.3) of any of the fabrics produced in this work, and this is substantially higher than has been previously reported in the literature. Fibrillation of the regenerated cellulose fibres was not observed under SEM to be present after hydroentanglement.

6.4.2 Tensile strength of wetlaid fabrics containing non-fibrillating fibres

Differences in the properties of airlaid-hydroentangled and wetlaid-hydroentangled fabrics were repeatedly observed during this study, even when

made from identical blend compositions. To understand if non-fibrillating fibres affect the tensile strength of wetlaid wipes, experimental fabrics were constructed from standard lyocell, Tencel A100 and viscose. Tencel A300 was not available in sufficient quantity to enable wetlaid processing so was excluded. The data relate to wetlaid fabrics of varying construction including fibre length (6 -10 mm), linear density (1.4-1.7 dtex) and process conditions (0.225 – 0.769 $MJ.kg^{-1}$). Details of the fibre composition and specific energies used to produce the samples are given in Table 6.4.

Table 6.4. Fibre composition and specific energies used to produce wetlaid-hydroentangled fabrics for tensile testing

Fibre Type	Linear Density (dtex)	Fibre Length (mm)	Specic Energy ($MJ.kg^{-1}$)
A100	1.4	6	0.225
A100	1.4	8	0.225, 0.769
A100	1.4	10	0.769
Tencel	1.7	6	0.225, 0.769
Tencel	1.7	8	0.225, 0.325, 0.473, 0.769
Tencel	1.7	10	0.769
Tencel	1.4	6	0.225, 0.769
Tencel	1.4	8	0.769
Tencel	1.4	10	0.769
Viscose	1.7	6	0.225
Viscose	1.7	8	0,225, 0.473, 0.769
Viscose	1.7	10	0.769

The results for dry MD breaking load are shown in Figure 6.14. Similar dry tensile strength values were observed irrespective of the type of regenerated cellulose fibre present in the blend. Noticeable differences in the spread of data

were observed. One-way ANOVA confirmed that the means were not significantly different ($p = 0.54$) at the 0.05 level.

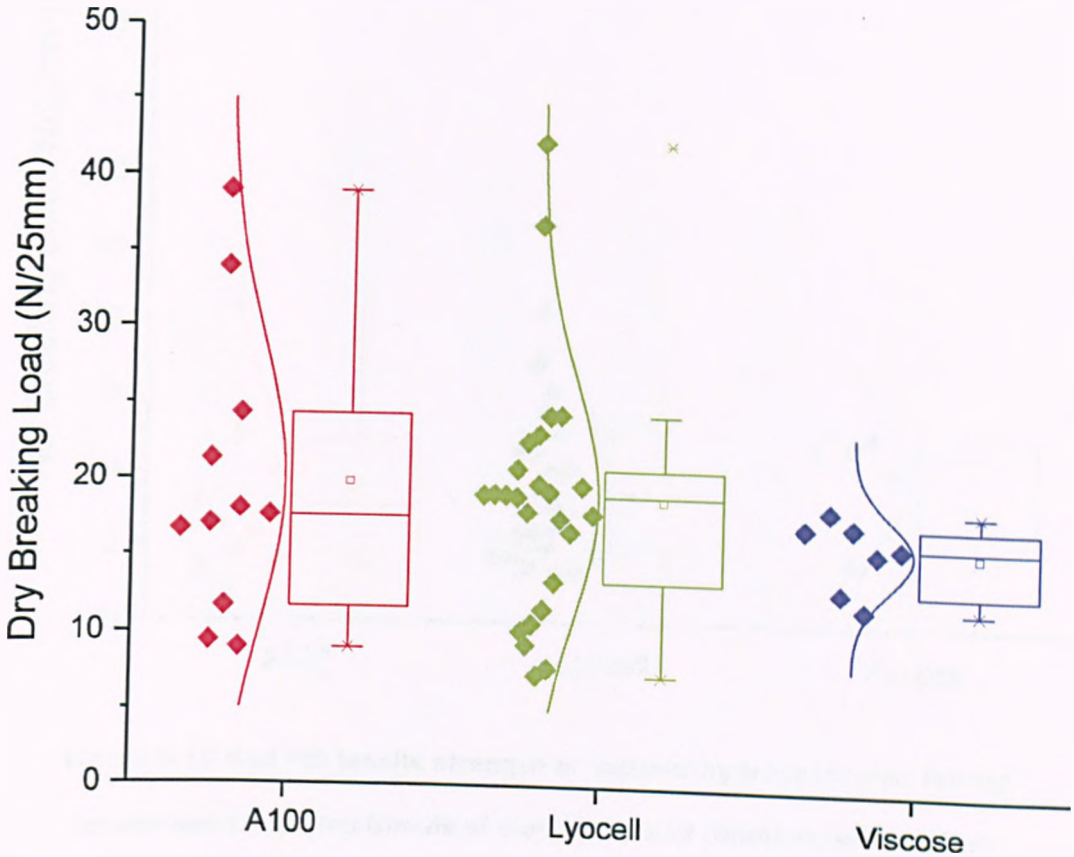


Figure 6.14. Dry MD tensile strength of wetlaid-hydroentangled fabrics comprised of blends of wood pulp and regenerated cellulose

The wet MD tensile strength of the wetlaid-hydroentangled fabrics are shown is Figure 6.15. The results are very similar for all the fibre variants and the means were not significantly different at the 0.05 level ($p = 0.78$). In absolute terms, the wet tensile strengths were much reduced in comparison to the dry shown in Figure 6.14, with only 18-26% of the dry strength being retained. This may be the result of hydrogen bonding influencing dry tensile strength of wetlaid fabrics, which is not retained once the fabrics are wet. Lumen collapse in the wood pulp upon drying thereby increasing contact area and propensity to hydrogen bonding would be expected to contribute to the dry strength (224).

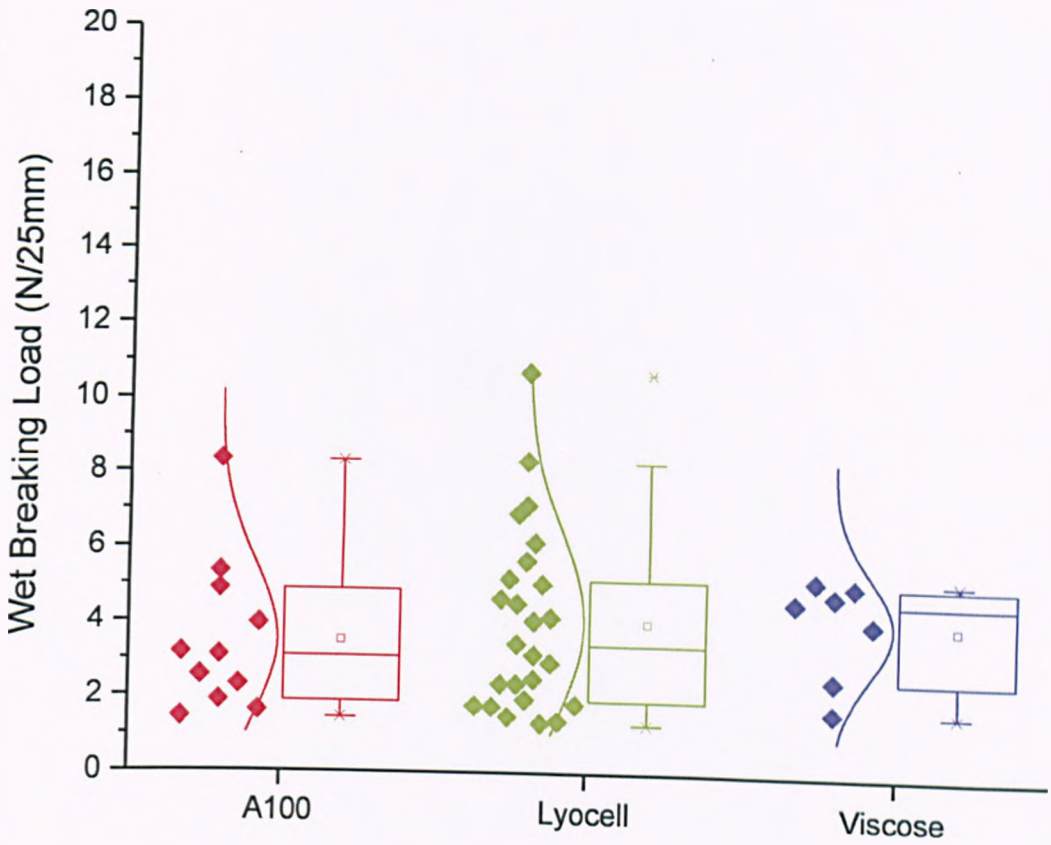


Figure 6.15 Wet MD tensile strength of wetlaid-hydroentangled fabrics comprised of varying blends of wood pulp and regenerated cellulose

To further understand the influence on tensile strength, wetlaid-hydroentangled fabrics were constructed using the same composition and process conditions, this time using non-fibrillating fibres as the regenerated cellulose blend component. The fabrics were all composed of 80% wood pulp and 20% 1.4 dtex regenerated cellulose fibre with the exception of viscose, which was only available in 1.7 dtex. All fabrics were hydroentangled at the same specific energy (0.769 $MJ.kg^{-1}$). The wet and dry MD tensile strength of wetlaid fabrics composed of 8 and 10 mm fibres are shown in Figure 6.16.

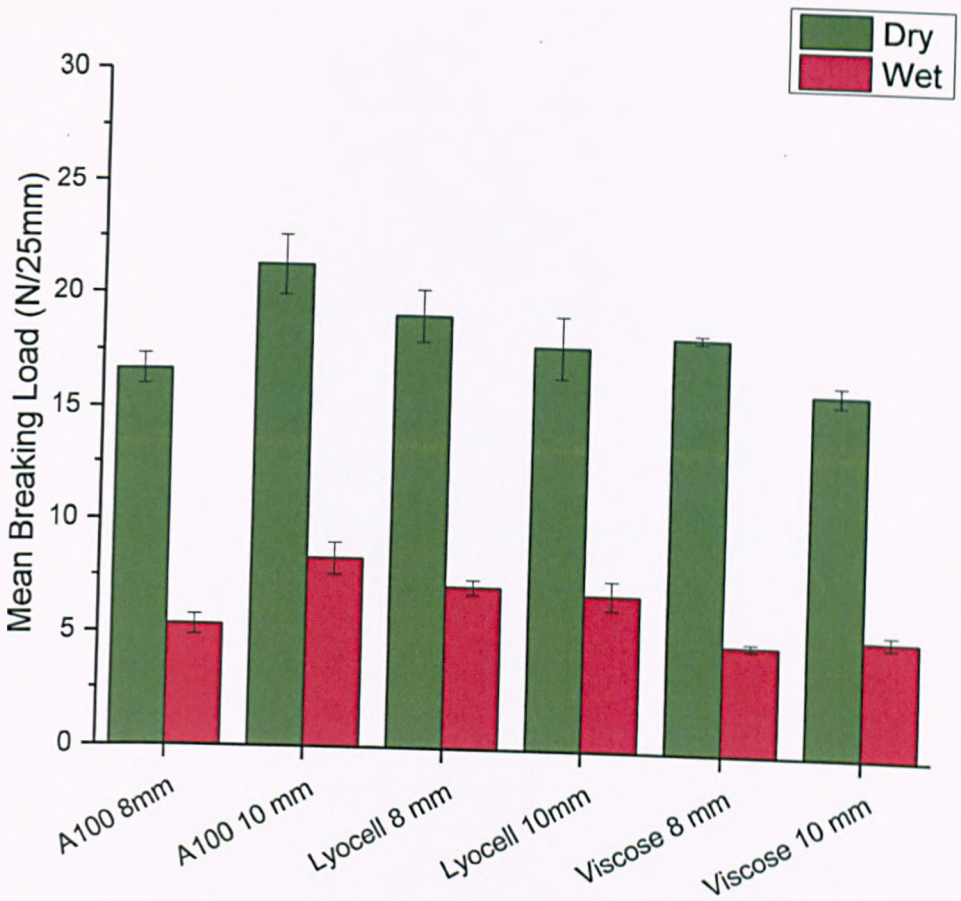


Figure 6.16 Wet and dry MD tensile strength of wetlaid 80:20 wood pulp-regenerated cellulose hydroentangled at 0.769 MJ.kg^{-1}

The dry tensile strength values varied, but not systematically in relation to fibre length. This implies the influence of a secondary bonding mechanism, such as hydrogen bonding, which is known to be present in cellulose pulp-rich wetlaid fabrics. The inclusion of viscose resulted in fabrics with the lowest wet strength, compared to other fibres of the same length. The fabric containing 10 mm Tencel A100 exhibited the highest wet tensile strength, as was observed in the airlaid-hydroentangled fabrics. Although Tencel A100 exhibits tensile strength approximately 10% lower than lyocell it is postulated that the frictional characteristics of A100 are altered during cross-linking, i.e. creating higher

friction, leading to an improvement in tensile strength in mechanically bonded fabrics.

The data comparing wet and dry MD tensile strength values with the dispersibility of wetlaid-hydroentangled fabrics shown in Figure 6.10 and Figure 6.16 is summarised in Table 6.5.

Table 6.5. Comparison of MD tensile strength and dispersibility of 80:20 wood pulp-regenerated cellulose hydroentangled at 0.769 MJ.kg^{-1}

Fabric composition	Dry breaking Load (N/25 mm)	Wet Breaking Load (N/25 mm)	Mean Clearance <12.5 mm (%)	Mean Clearance <3.15 mm (%)
A100 8mm	16.66	5.33	98.88	98.22
A100 10 mm	21.29	8.33	95.58	93.25
Lyocell 8 mm	19.13	7.16	99.13	94.41
Lyocell 10 mm	17.89	6.93	77.59	74.24
Viscose 8 mm	18.40	4.86	99.98	99.92
Viscose 10 mm	16.07	5.26	97.21	91.70

It can be observed in Table 6.5 that the fabric containing 10 mm Tencel A100 exhibited the highest wet tensile strength but also maintained a high level of dispersibility (>93% cleared the 3.15 mm screen), greater than all the fabrics comprising 10 mm regenerated cellulose fibre. It is plausible that difference in modulus between Tencel A100 and other lyocell variants enables higher levels of entanglement to be generated during hydroentangling, producing greater wet strength. Despite the enhanced entanglement, dispersibility is maintained

compared to standard lyocell because of the excellent fibrillation resistance of the A100 fibre.

6.5 Summary

Fibre fibrillation has been found to have a profound effect on the dispersibility of both wetlaid and airlaid hydroentangled fabrics. Of the various non-fibrillating lyocell fibres studied, Tencel A100 was found to be the only variant that resisted fibrillation when fabrics were subjected to the conditions prevailing in shake flask dispersibility testing. The inherently greater resistance of the Tencel A100 fibre to fibrillation was also confirmed in CSF testing. The Tencel A300, Tencel A300(2) and standard lyocell fibres were susceptible to fibrillation during shake flask agitation, and it is believed that this fibrillation impeded the release of fibres and fragmentation of the wipe substrate, negatively affecting dispersibility.

Therefore, directly substituting standard lyocell with Tencel A100 in blends with wood pulp leads to improved dispersibility, particularly in airlaid-hydroentangled fabrics. Because in general the dispersibility of wetlaid-hydroentangled fabrics was excellent, the benefit of substituting Tencel A100 for standard lyocell fibres was discernibly less pronounced.

The dispersibility of airlaid and wetlaid fabrics differed with the wetlaid fabrics showing better dispersion. This can be attributed to the differences in structure resulting from the two web forming techniques. The airlaid web is more open and less planar after formation, and as such fibre movement is less restricted

and fibres can entangle more efficiently. Conversely, the wetlaid structure is denser and more planar, due to hydraulic force applied during fibre deposition, which results in less fibre entanglement in the final fabrics for the same applied specific energy.

Differences in wet tensile strength alone does not account for the differences in dispersibility observed in Figure 6.7 and Figure 6.10, suggesting that the fibrillation resistance does contribute to the wet disintegration of the wipe substrates. To test this theory the CSF after 60 min was plotted against the mean clearance <12.5mm for fabrics containing 10 mm fibres. The results are shown in Figure 6.17.

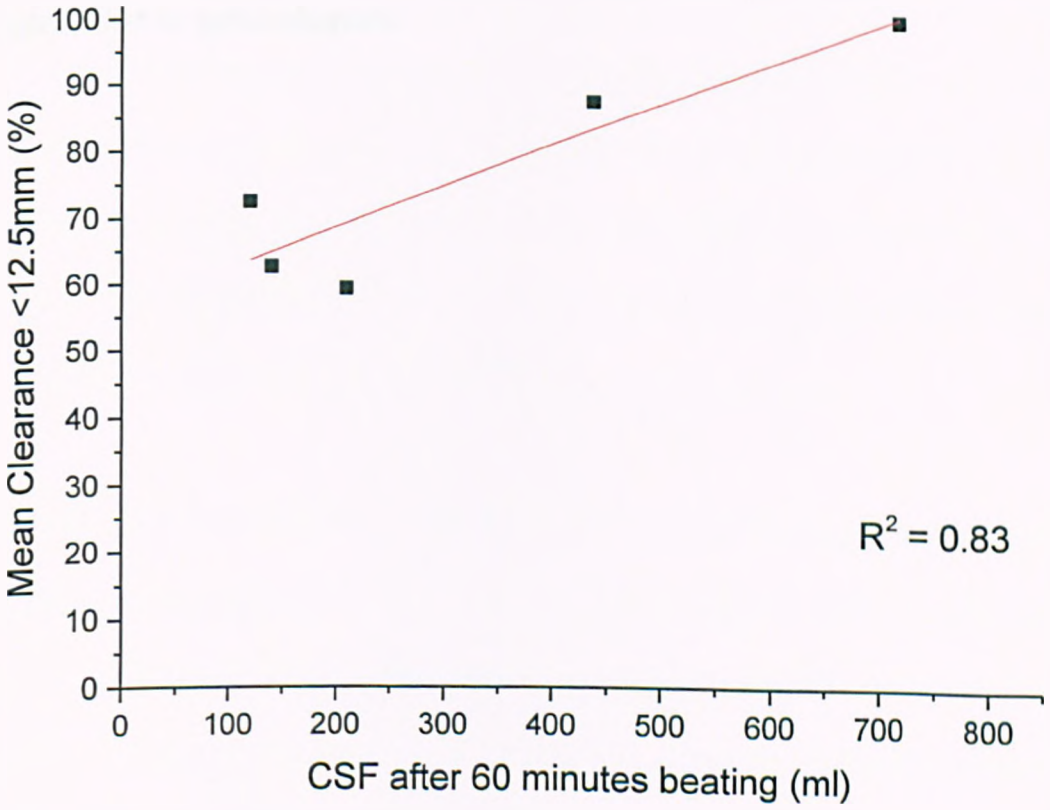


Figure 6.17. Plot of mean clearance (<12.5mm) against CSF showing an approximate linear relationship

There is a linear relationship between CSF after 60 min beating and the mean clearance <12.5mm (R^2 = 0.83). The fibres with a higher propensity to fibrillate in the CSF test were also those that did not disperse well when converted in to fabric. Collectively, there is therefore evidence to suggest that fibre fibrillation during the shake-flask test is likely to lead to a reduction in fabric dispersibility. These observations also raise questions about the suitability of a shake-flask test in an industry-wide standard method for measuring dispersibility, particularly if it involves vigorous agitation for an extended period of hours. In this test, fabrics containing fibres such as standard lyocell, that are known to be susceptible to fibrillation, may be unduly categorised as having poor dispersibility, whereas a real pipeline and sewer system their disintegration might in fact be quite adequate.

Chapter 7

Application of Auxiliary Chemistry to Mechanically-bonded Wipes

7.1 Introduction

The review in Chapter 2 identified three main commercially applicable approaches for the bonding of flushable wipe fabrics: mechanical bonding (most commonly via hydroentanglement), adhesive bonding and combinations of mechanical and adhesive bonding. The use of a wetting medium (lotion) that controls the adhesive strength of a chemical binder applied to the fabric has been previously exploited as a means to trigger disintegration of wipe fabrics at the point of disposal. Therefore, in this chapter it was of interest to determine the degree to which the balance of wet tensile strength and dispersibility of fabrics could be controlled by the addition of auxiliary chemistry, either as part of the fibre or applied to the finished fabric.

Wastewater systems are principally designed to deal with human excreta and cellulose in the form of toilet paper. For this reason a chemical adhesive (binder) material based on cellulose was explored, specifically carboxymethyl cellulose (CMC). CMC has been previously used in flushable product applications (108, 262) and is produced on a cost-effective industrial scale. CMC is also of interest in the design of water dispersible nonwoven wipes, because its physical properties and adhesive behaviour are known to be

influenced by common salts such as sodium chloride, and changes in the pH of the surrounding liquid medium (263).

Initially, to understand the behaviour of CMC adhesively bonded fabrics, short-fibre airlaid-hydroentangled fabrics composed of wood pulp and regenerated cellulose fibre were print-bonded or saturation bonded with CMC in an effort to enhance the wet tensile strength when salted-out with an electrolyte-containing lotion. It was reasoned that any additional strength would then be subsequently reduced after placing the fabric in an aqueous medium by diluting the electrolyte and increasing the solubility of the binder. Furthermore, by adjusting the volume of wetting liquid (lotion) applied to the fabric volume, the pH of the lotion and the concentration of electrolyte, it was anticipated that wet fabric strength and dispersibility could be controlled. In these experiments the effect of the molecular weight and the degree of substitution of the CMC was also studied. Preliminary work was also completed in which CMC was incorporated within the regenerated fibres themselves to determine if this could provide a new route to exploit the salting-out mechanism.

7.2 Materials and experimental plan

Table 7.1 details all the fibres used in this part of the study and includes a number of new proprietary fibres containing CMC that were prepared by Lenzing specially for this work. All regenerated cellulose fibres were crimped to ensure compatibility with the airlaid process.

Table 7.1. Fibre materials used to make airlaid-hydroentangled pulp-regenerated cellulose experimental wipes containing CMC

Fibre Type	Fibre length (mm)	Linear density (dtex)	Supplier
Lyocell (Tencel)	6	1.4, 1.7	Lenzing
Viscose	6	1.7	Lenzing
Wood pulp (Golden Isles Fluff Fully Treated - HA Grade 4822	2.4		GP Cellulose LLC
Viscose extruded with CMC, 1%	6	1.7	Lenzing
Viscose extruded with CMC, 3%	6	1.7	Lenzing
Viscose extruded with CMC, 5%	6	1.7	Lenzing
Lyocell extruded with CMC, 1%	6	1.7	Lenzing
Lyocell extruded with CMC, 3%	6	1.7	Lenzing
Lyocell extruded with CMC, 5%	6	1.7	Lenzing

Table 7.2 specifies the auxiliary chemicals and wet wipe lotions utilised in the manufacture of the wet wipe substrates. Nice-Pak International, one of Europe's largest wet wipe manufacturers, supplied a commercially used Moist Toilet Tissue (MTT) lotion.

Table 7.2. Chemicals used for the preparation of experimental wet wipes

Type	Grades	Supplier
Moist Toilet Tissue Lotion	104330	Nice-Pak International
Carboxymethyl Cellulose	Niklacell T30G, T50G, T100G, DS 0.4, DS 0.55	Mare
Carboxymethyl Cellulose	Cekol 500, 30000, 50000	CP Kelco
Carboxymethyl Cellulose	Walocel 2000, 60000	CP Kelco
Carboxymethyl Cellulose	Finnfix 500, 700, 10000, 30000	Dow
Sodium Chloride	Reagent grade	Sigma Aldrich
Sodium Carbonate	Anhydrous ≥99.5%	Sigma Aldrich
Calcium Chloride	Anhydrous, ≥97%	Sigma Aldrich

7.2.1 Application of CMC to airlaid-hydroentangled fabrics

Hydroentanglement generates mechanical entanglements between fibres in the fabric, which ideally need to disentangle if the fabric is to properly disintegrate when it is disposed of in the sewer network. Another option is to introduce a smaller degree of mechanical entanglement during hydroentanglement and then to apply an adhesive in a second processing step, which increases the strength of the substrate using an adhesive. According to the literature (108, 136, 262) Carboxymethyl Cellulose (CMC) is a suitable binder because its adhesive strength can be made to vary depending upon the salt content of the liquid medium into which it is placed. Liquid medium in this context refers to the lotion (present during use of the substrate) and to toilet water (present during disposal of the substrate).

The substrates used for this study were all airlaid and hydroentangled blends of woodpulp and lyocell or Tencel A100 (80:20 or 70:30). The linear density varied between 1.4-1.7 dtex, the fibre length between 6 or 8 mm and the specific energy applied was either 1.192, 5.52 or 6.85 $MJ.kg^{-1}$.

Impregnation of the wipes with the CMC was achieved using a Xiamen Rapid Company mangle applicator, a schematic representation is shown in Figure 7.1.

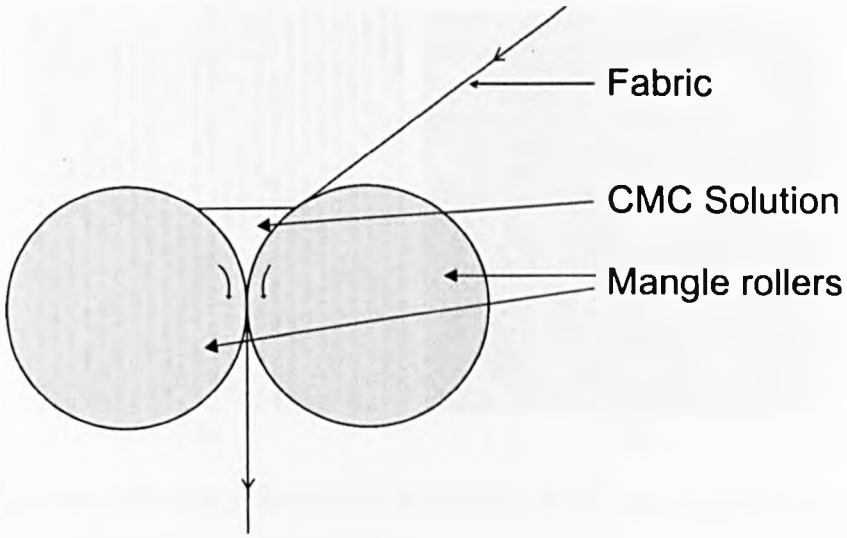
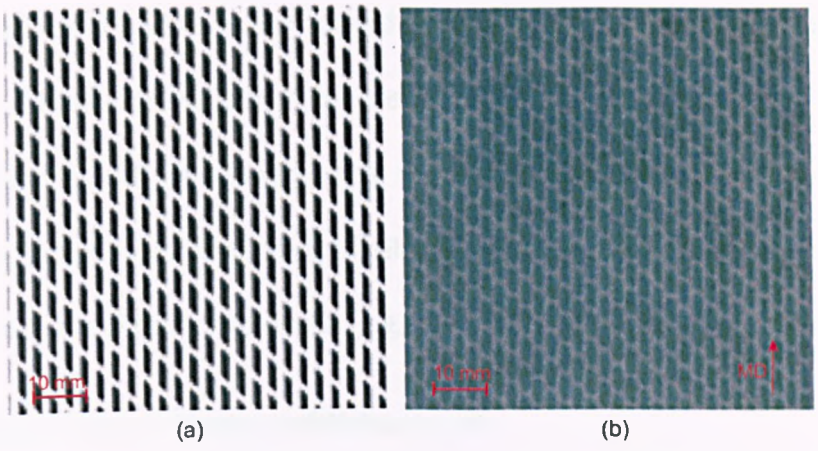


Figure 7.1. Schematic representation of mangle applicator used for applying CMC solution to airlaid-hydroentangled wipes

The CMC solution was applied between the rubber coated rollers set at a nip pressure of 1 bar at a speed of 1 $m.min^{-1}$. The nonwoven was passed through the CMC solution and subsequently dried at 100°C for 300 s in a Spooner through-air oven set to a fan speed of 40%.

Because CMC is a relatively stiff polymer, a continuous coating of this material on the fabric could lead to a very rigid substrate, which is obviously not acceptable to produce a wipe acceptable to a consumer. Accordingly, to maintain flexibility in the substrate, CMC was also screen printed onto pre-formed airlaid-hydroentangled fabrics using a parabolic pattern as shown in Figure 7.2.



(a) Pattern applied to the printing screen; (b) Printed CMC on the nonwoven substrate

Figure 7.2. Print-bonding pattern

Print formulations were prepared from 5% w/v CMC, which was dissolved in deionised water, heated to a temperature of 60°C to ensure complete solvation. This concentration of CMC solution was selected to provide sufficient viscosity suitable for screen printing. Several CMC grades were investigated (Table 7.2). A small amount (0.1g) of green pigment (Dystar, Imperon Green KG) was added to 200 ml of coating formulation to enable visual assessment of the CMC coating once transferred to the fabric. A 25 ml sample of the 5% w/v CMC solution was then screen printed onto one side of the specimen using a print area of 270 x 185 mm, applying 25 $g.m^{-2}$ dry weight of CMC to the fabric. The fabrics were subsequently dried at 100°C for 300 s in a Spooner through-air oven set to a fan speed of 40% for 8 minutes.

7.3 Modification of the wetting liquid

The lotion is an integral component of any flushable wet wipe system. In practice, nonwoven wipe substrates are pre-loaded with lotions such as oil in water emulsions, aqueous solutions or organic solvents (242). In moist

flushable wipes the lotions are intended to aid the removal of contaminants from the surfaces to which they are applied and it is expected that any deposited lotion will be subsequently removed by additional wiping. For skin contact applications, such as Moist Toilet Tissue, the lotion should also comply with industry regulatory standards (e.g. cosmetic regulations) and be skin-safe.

7.3.1 Modification of lotion addition level

The industry-standard addition level of lotion is regarded as 250-400% by weight of the wipe (131, 168, 264). To determine if lotion saturation affects the wet tensile properties of the fabric the addition level of lotion was varied and the wet strength measured using the strip tensile method detailed in section 3.3.2. Airlaid-hydroentangled fabrics were produced using a blend of 30% 1.4 dtex, 8mm Tencel A100 and 70% wood pulp and specific energy during hydroentangling was 1.192 $MJ.kg^{-1}$. The MD tensile data was normalised by fabric weight to provide specific strength data for comparison. The results are shown in Figure 7.3.

It was evident that the level of saturation by the lotion influences wet fabric tensile strength, although the effect is small in the range that is practically relevant of 250-350% by weight. Beyond 350% a substantial decrease in wet tensile strength was observed.

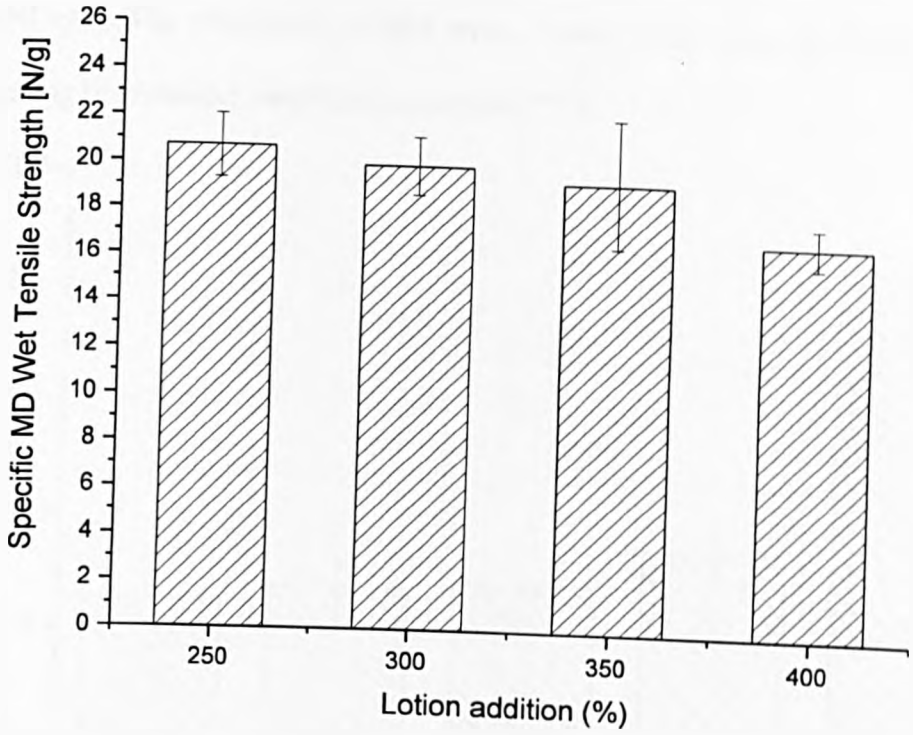


Figure 7.3. Effect of lotion addition on wet MD tensile strength of airlaid-hydroentangled wipes made of 70% pulp/30% 8mm Tencel A100

The lotion composition, given in Table 3.4, includes 0.75% of surfactant, which could potentially affect the frictional characteristics of fibres. In all the experiments that follow the lotion addition levels were 300-350% w/w.

7.3.2 Modification of electrolyte concentration

The concentration of electrolyte in the lotion is of particular importance to ensure a measurable increase in wet tensile strength after the CMC application. Whilst increasing the electrolyte content of the lotion is preferable in terms of maximising wet strength, practically it needs to be minimised to prevent skin irritation and corrosion of the processing machinery during wet-wipe manufacture. Figure 7.4 illustrates the effect of increasing the concentration of sodium chloride (NaCl) in the lotion on the wet MD tensile strength of experimental CMC printed wipes (80:20 wood pulp:lyocell, 1.7 dtex, 6mm, SE =

6.85 MJ.kg^{-1}). The wipe was printed with a solution of 5% w/v CMC (Finnfix 700) using the method described in section 7.2.1.

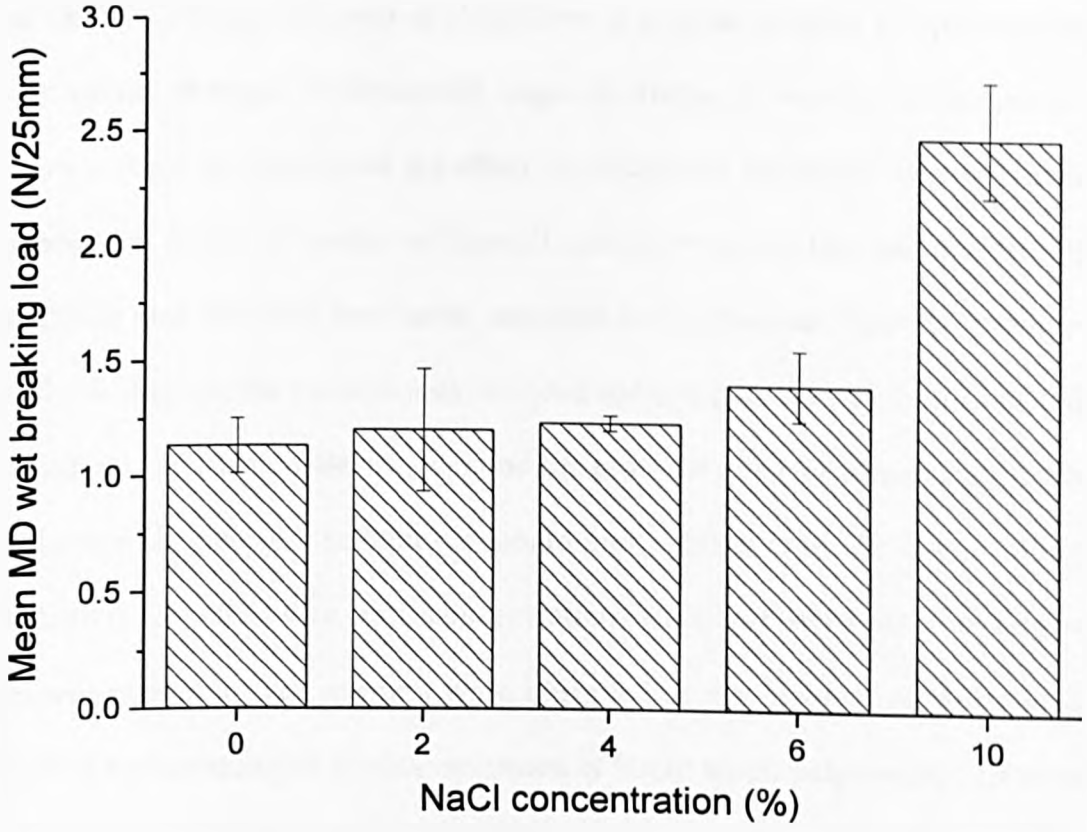


Figure 7.4. Change in wet MD tensile strength of CMC printed wood pulp-lyocell (1.7 dtex, 6mm) hydroentangled fabrics with increasing salt (NaCl) content in the wetting liquid.

A significant increase in the MD wet strength of the wipe was apparent at higher concentration, particularly between 6% and 10% w/v (0.05 level; $p = 0.026$). This can be attributed to an increase in the degree of salting-out of the CMC binder, i.e. the CMC is less able to dissolve and remains solid maintaining the interfacial bonds between adjacent fibres. Although 10% NaCl w/v may produce a wet tensile strength that is adequate in use, problems with metal corrosion in industrial processes have been reported using such concentrations (251).

7.3.3 Effect of electrolyte type

The type of electrolyte present in the lotion can affect the salting out properties of CMC. By varying the type of electrolyte, it may be possible to optimise the wet tensile strength of dispersible wipe substrates. A number of electrolytes were studied to understand the effect of salting-out behaviour on wet tensile properties. From the studies of Randall and Failey (163), the best performing negative ions included hydroxide; sulphate and carbonate; chlorate, bromate and chloride and the positive ions included sodium, potassium, lithium, barium, rubidium and calcium. Bearing in mind the practical need for skin compatibility, only sodium chloride, sodium carbonate and calcium chloride were studied. Solutions of 10% w/v salt concentration were prepared as the largest improvements in wet strength were observed at the highest concentrations. Airlaid-hydroentangled fabrics composed of 80:20 wood pulp:lyocell (1.7 dtex, 6mm) were produced using 5.52 $MJ.kg^{-1}$ specific energy. A 0.05% w/v CMC (Niklacell T30G) solution was impregnated onto the fabric using a pad mangle applicator as described in section 7.2.1. This method of application was selected in preference to printing to enable a lower addition level of CMC to the wipe fabrics to maximise the ratio of carboxyl groups in the CMC to sodium ions in the electrolyte.

The results in Figure 7.5 indicate that sodium chloride produced significantly higher MD wet tensile strength, compared to the carbonate salt of sodium or calcium chloride (0.05 level; $p = 0.006$).

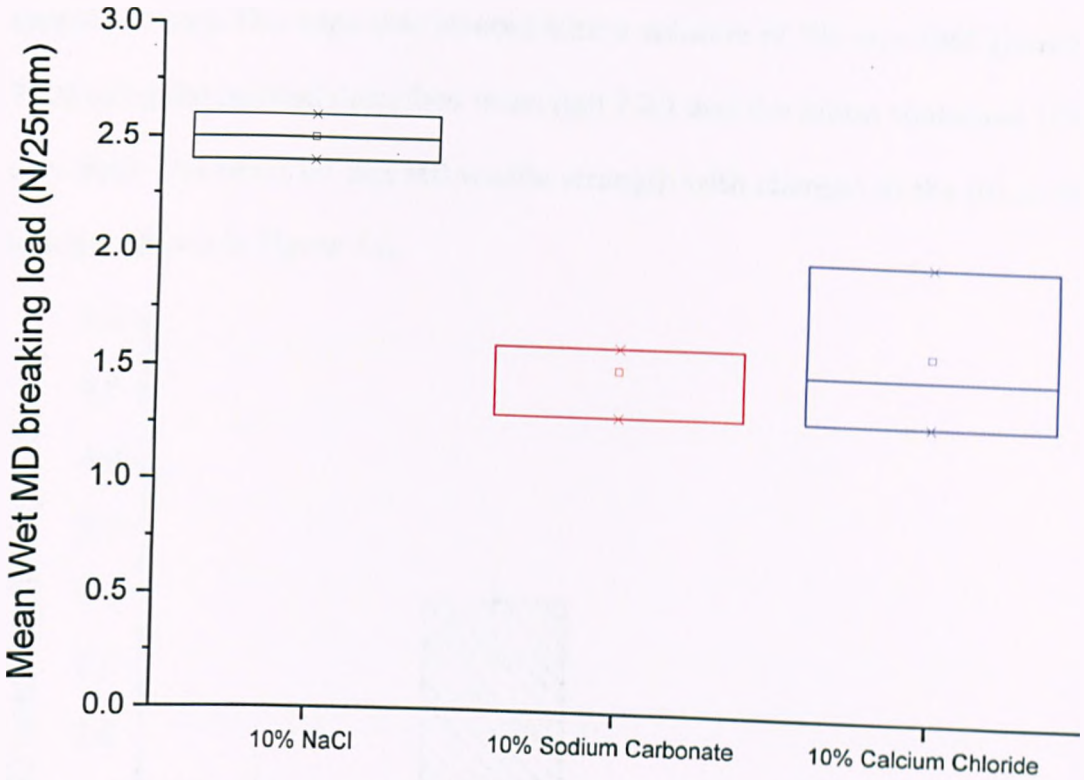


Figure 7.5. Effect of electrolyte type on MD wet tensile strength of wood pulp-lyocell (1.7 dtex, 6 mm) on CMC-impregnated airlaid fabrics

The salting-out performance was apparently contrary to the findings of Randall and Failey who suggested that carbonate ions should exhibit the greatest salting out performance (163).

7.3.4 Modification of pH of wetting liquid

The pH of the lotion is important for skin health but is also likely to influence the salting out reaction and resultant wet tensile strength. The pH of the commercially available lotion used in these experiments was initially pH 5.4, but was subsequently modified to between pH 4-8 to understand the effect of changing pH using dilute solutions of sodium hydroxide and sulphuric acid. This pH range was selected because these values are considered most suitable for skin contact applications (264). Airlaid-hydroentangled fabrics composed of 80:20 wood pulp:lyocell (1.7 dtex, 6mm) were produced using 6.85 $MJ.kg^{-1}$

specific energy. The wipe was printed with a solution of 5% w/v CMC (Finnfix 700) using the method described in section 7.2.1 and the lotion contained 10% w/v NaCl. The effect on wet MD tensile strength with changes in the pH of the lotion is shown in Figure 7.6.

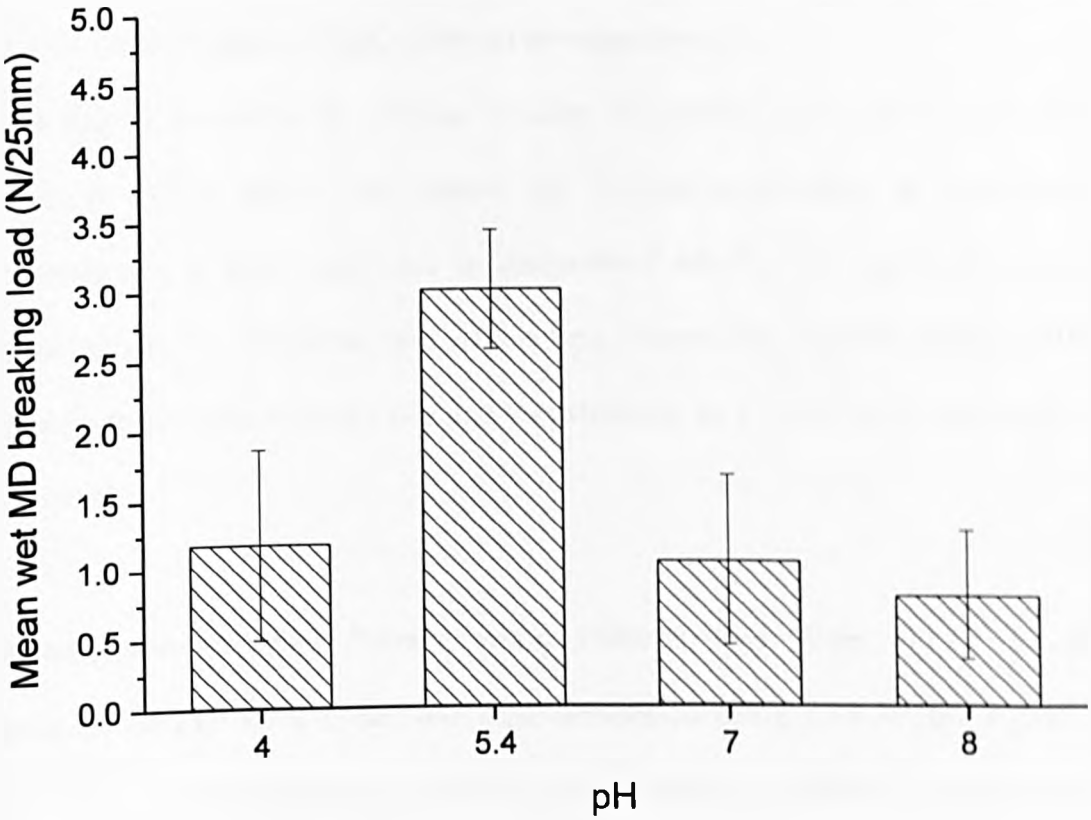


Figure 7.6. Effect of lotion pH on wet MD tensile strength

In Figure 7.6 it may be observed that the wet tensile strength is highest at pH 5.4 and increasing or decreasing the pH results in a reduction in the wet tensile strength. This finding agrees with the work of Shimizu and Takeuchi et al. who recommended a pH of a least 5 for a CMC-based binder (108, 175).

7.4 Modification of CMC polymer

Having established the effects of lotion composition on resultant wet tensile strength, the effect of CMC parameters were investigated. Variations in

molecular weight, degree of substitution, as well as the addition of the CMC during regenerated cellulose fibre manufacture were explored. The contribution of the CMC addition to overall wet strength of the fabric was then determined.

7.4.1 Contribution of CMC addition to wipe strength

The degree to which the addition of CMC can contribute to the overall wet strength of a fabric pre-bonded by hydroentanglement is unknown. Accordingly, it was instructive to understand whether or not a twin-step bonding strategy involving hydroentangling followed by print bonding of CMC could substantially enhance dry and wet strength, as a result of the salting out mechanism.

Airlaid-hydroentangled fabrics were manufactured from 80:20 wood pulp:lyocell (1.7 dtex, 6mm) and hydroentangled using 6.85 $MJ.kg^{-1}$ specific energy. The substrates were printed using either 5% w/v CMC or impregnated with a 0.1% w/v CMC solution (both Finnfix 700). 10% w/v NaCl was added to the wetting lotion. The dry and wet MD tensile strength results are shown in Figure 7.7. Contrary to the published literature (108, 174, 262), printing of the CMC binder onto pulp-lyocell fabrics did not lead to substantial increases in tensile strength and only modest increases in dry strength in both the MD and CD were observed.

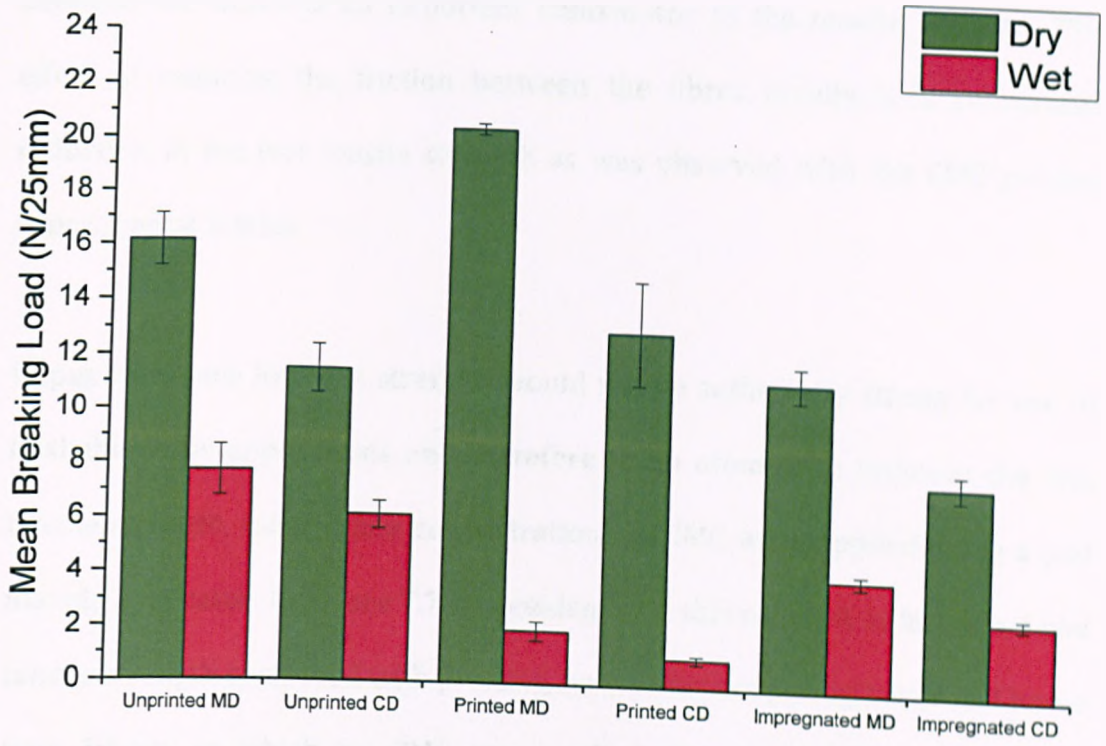


Figure 7.7. Comparison of the MD tensile strength of wood pulp-lyocell (1.7 dtex, 6 mm) airlaid-hydroentangled fabrics before and after printing or impregnation with CMC

Comparing breaking load in the wet state for the unprinted samples, it may be observed that the strength decreased by more than 50% in the MD direction but to a lesser extent in the CD direction. This is not unexpected as the tenacity of many cellulosic fibres reduces substantial in aqueous conditions (Table 2.4).

Surprisingly, the wet strength decreased considerably when CMC was applied to the fibres, possibly due to a decrease in the coefficient of friction between the fibre surfaces. It was observed that, even with the addition of 10% w/v NaCl to the wetting lotion, the fabric felt slippery compared with the unprinted samples. It was highlighted in section 5.4 that because the fabric is bonded mainly by mechanical means, using very short fibres, the frictional resistance

between the fibres is an important contributor to the tensile strength. The effect of reducing the friction between the fibres results in a substantial reduction in the wet tensile strength as was observed with the CMC printed experimental fabrics.

Wipes with such low wet strength would not be sufficiently strong for use in flushable wipe applications and therefore in an attempt to improve the wet tensile strength, more dilute concentrations of CMC were applied using a pad mangle applicator. In Figure 7.7 it is evident that this resulted in increased wet tensile strength compared with printing, but the tensile strength was still lower than fabrics in which no CMC was applied. This particular impregnation method was used to apply CMC to the fabrics in all of the following experiments.

7.4.2 CMC of varied molecular weight

The strength of paper has been shown to improve by increasing the molecular weight of the applied CMC binder (265). It is reasonable to expect a similar effect in cellulose-based nonwovens. To understand if the molecular weight of CMC influences the salting-out behaviour of the polymer and therefore the wet tensile strength, a range of commercially available CMC's were sourced of varying molecular weights: including Finnfix 500T, Finnfix 700, Finnfix 30000, Finnfix 10000, Cekol 30000 A, Cekol 50000, Walocel 60000, Walocel 2000. The molecular weight varied between 190000-1100000 $g.mol^{-1}$. Airlaid-hydroentangled fabrics were produced from 80:20 wood pulp:lyocell (1.7 dtex, 6mm) were produced using 6.85 $MJ.kg^{-1}$ specific energy. A 0.1% w/v solution was impregnated using the pad mangle method described in section 7.2.1. 10%

w/v NaCl was applied to the lotion. The degree of substitution was between 0.7-0.9. The wet MD tensile strength results are shown in Figure 7.8.

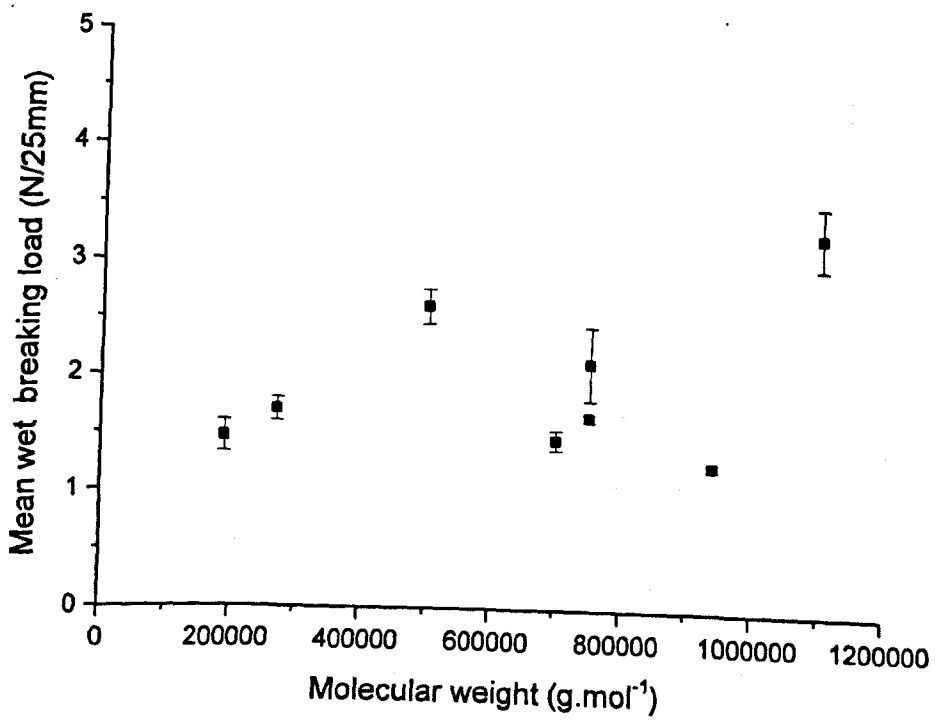


Figure 7.8. Influence of CMC molecular weight on wet MD tensile strength of airlaid-hydroentangled fabrics produced from 80:20 wood pulp:lyocell (1.7 dtex, 6mm)

Figure 7.8 shows limited correlation between CMC molecular weight and mean wet tensile strength suggesting that the salting-out behaviour of CMC is not strongly influenced by molecular weight. It is possible that differences in the viscosity of the CMC formulations as a result of the molecular weight differences, could have affected the take up of the CMC by the substrate during impregnation.

7.4.3 Influence of CMC degree of substitution

The degree of substitution (D.S.) of CMC can potentially influence wet tensile strength (105, 108, 175) The D.S. is defined as the average number of substituted hydroxyl groups per glucose unit. An idealised unit structure of

CMC with a D.S. of 1.0 is depicted in Figure 7.9. Substitution of the remaining two hydroxyl groups would result in a D.S. of 3.0, the theoretical maximum. In practice, many of the commercial CMC grades vary between D.S. 0.5 - 1.5 as water solubility is affected below 0.6 and at 0.2 is rendered completely insoluble (266).

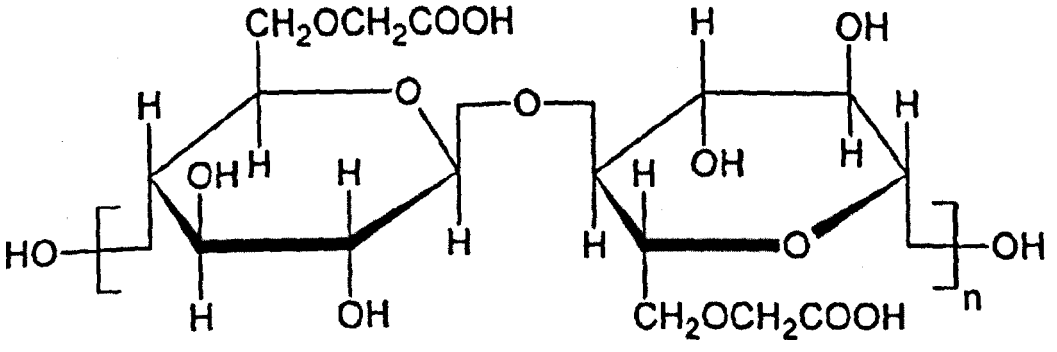


Figure 7.9. Chemical structure of CMC with D.S. of 1.0, adapted from Hoefler (267)

It is thought that the use of CMC polymer with a low degree of substitution (0.3-0.6) will influence solubility and wet tensile strength (108, 175). Consequently, the effect of changing the D.S. was explored and the wet MD tensile strength results are shown in Figure 7.10. These data relate to airlaid-hydroentangled fabrics made of 80:20 wood pulp:lyocell (1.7 dtex, 6mm) produced using 5.52 $MJ.kg^{-1}$ specific energy. The specific energy was lowered from 6.85 $MJ.kg^{-1}$ to reduce the variation in tensile properties of the airlaid-hydroentangled fabrics. Commercially available CMC's with differing D.S. values were sourced and applied with a mangle applicator using a of 0.1% w/v concentration solution, as described in 7.2.1. 10% w/w NaCl was added to the wetting lotion, of which 300-350% w/w was applied to the dry airlaid-hydroentangled fabrics post CMC addition.

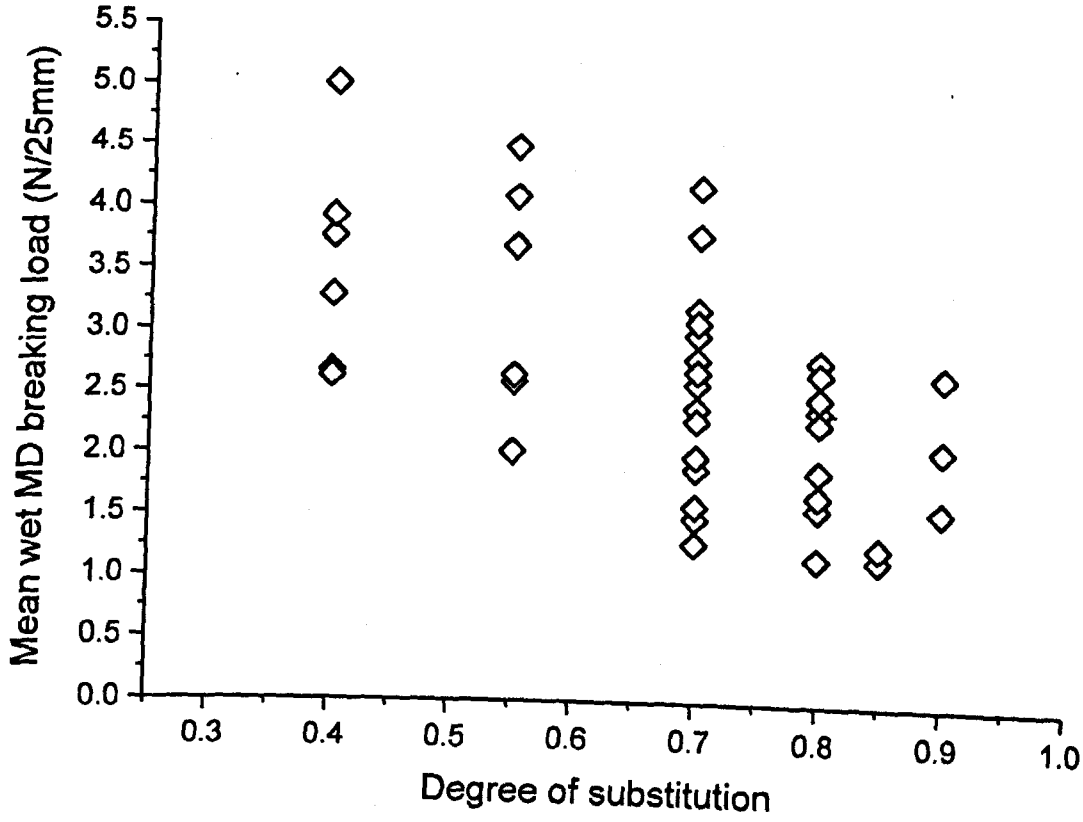


Figure 7.10. Influence of degree of substitution on MD wet tensile strength of airlaid-hydroentangled fabrics, 80:20 wood pulp:lyocell (1.7 dtex, 6mm)

There was a general trend for the MD wet tensile strength to increase with a decrease in D.S., which has also been confirmed by Takeuchi et al (175). Fabrics impregnated with 0.4 D.S. CMC exhibited the highest wet tensile strength. Reducing the degree of substitution will result in fewer carboxyl groups on the cellulose glucose unit, increasing the ratio of carboxyl groups to sodium ions in the electrolyte. Salting out of the CMC increases for the same level of electrolyte imparting greater levels of insolubility and hence increased wet tensile strength.

7.5 The dispersibility of CMC containing fabrics

The influence of CMC on the dispersibility of nonwoven fabrics is largely unreported in the academic literature. Previous work has focused on wet strength but did not measure corresponding dispersibility (175, 262). Given the reduction of wet tensile strength observed associated with CMC application in Figure 7.7, it is plausible to anticipate that the addition of CMC could improve dispersibility due to a reduction in fibre-fibre friction. To investigate the influence of CMC addition on dispersibility wood pulp-lyocell airlaid-hydroentangled fabrics (80:20, 6mm, 1.7 dtex, SE 6.85 $MJ.kg^{-1}$) were produced. Four fabrics were prepared: (a) with no CMC; (b) printed with 5% w/v CMC (Finnfix 700, D.S 0.8); (c) impregnated with 0.025% w/v Niklacell DS 0.4 and (d) impregnated with 0.025% w/v Niklacell DS 0.55 CMC. Each was subjected to 6 hr dispersibility testing using the shake flask method described in section 3.3.1. 10% w/v NaCl was added to the lotion. The results are shown in Figure 7.11.

There was a noticeable difference between the dispersibility of fabrics produced with no CMC compared with fabrics printed or impregnated with CMC, suggesting CMC addition has an influence on the final dispersion characteristics. One-way ANOVA revealed that the means were significantly different at the 0.05 level ($p = 0.0159$).

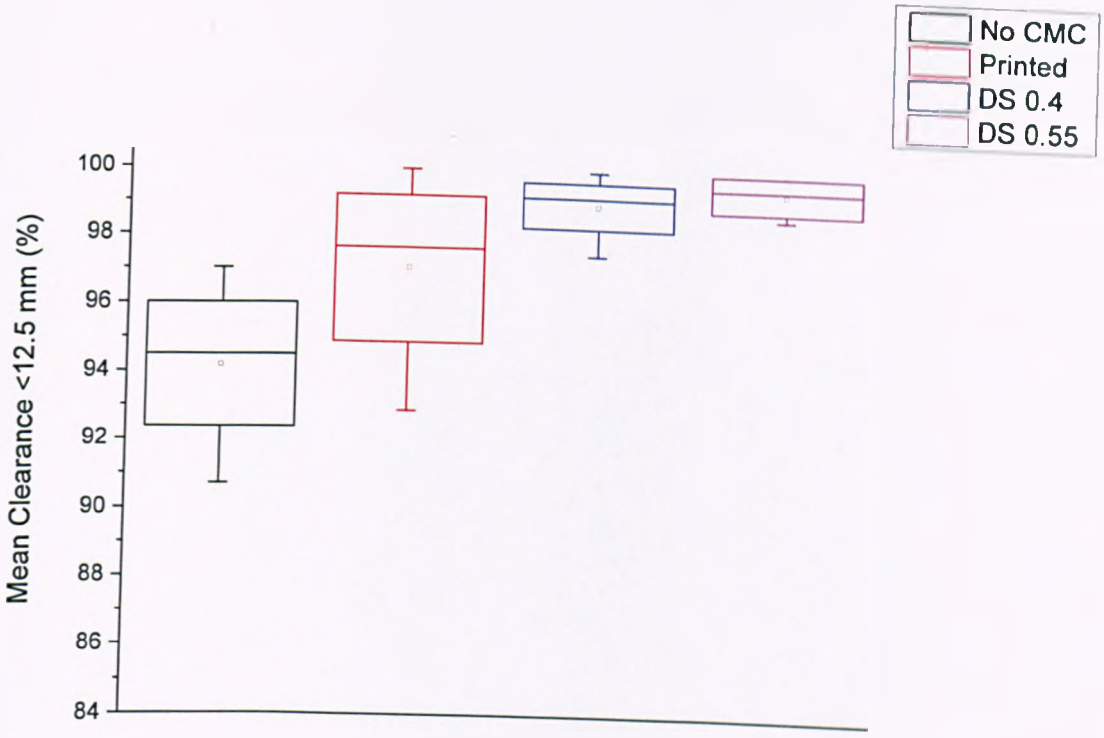


Figure 7.11. Influence of CMC on dispersibility of 80:20 wood pulp-lyocell (6mm, 1.7 dtex) fabrics showing increased dispersion with CMC addition

Impregnating the fabric with CMC evidently provided more uniform and consistent dispersion performance, which suggests that coating all the fibre surfaces rather than discrete areas maximises the modification of wet fibre friction and enables the fabrics to disintegrate more uniformly. The full dispersibility profiles are illustrated in Figure 7.12.

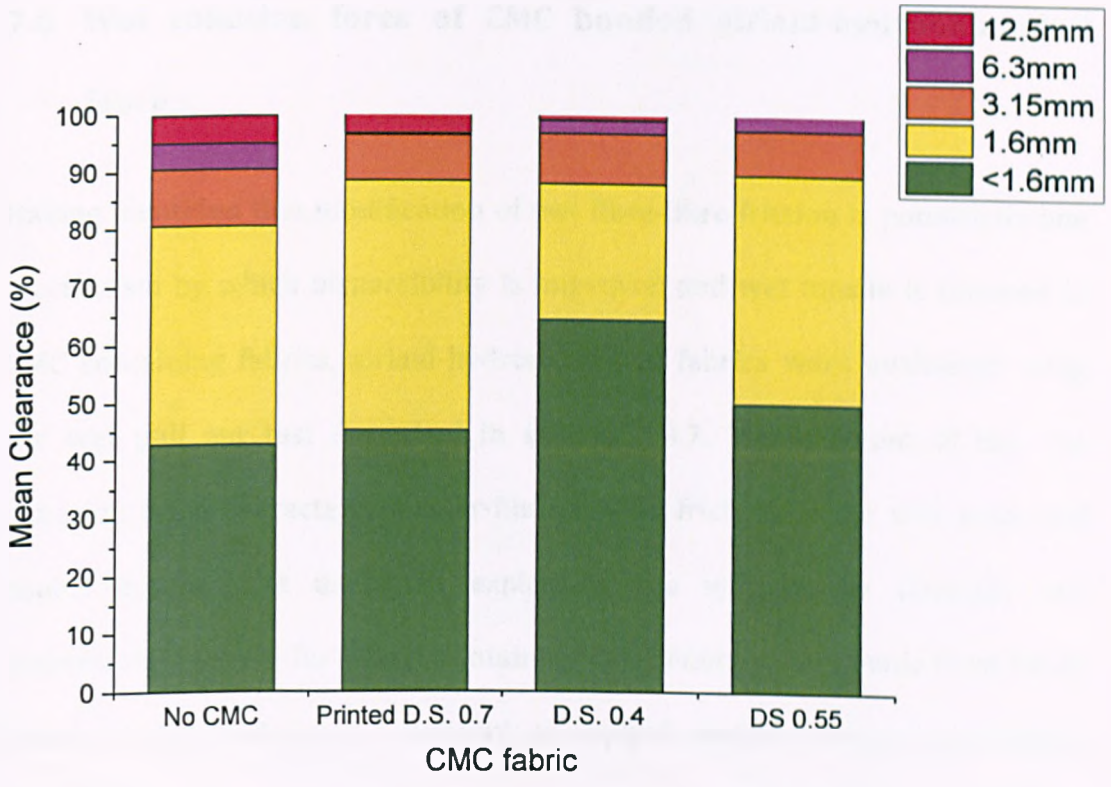


Figure 7.12. Dispersibility of airlaid-hydroentangled fabric showing increased dispersion with CMC addition

Fabrics containing no CMC produced greater levels of fibre capture in the largest two screens (12.5 and 6.3 mm), suggesting poorer separation of the fragmented fabric during the dispersibility test. Once CMC is applied, the dispersibility improved but the degree of disintegration was similar despite the method of application or degree of substitution of the CMC. Impregnation rather than printing of the CMC resulted in slightly improved dispersion with almost no fibre captured in the 12.5 mm screen. It may be speculated that the CMC has a lubricative effect on the fibre surfaces, providing the means for inter fibre friction to be overcome more readily during agitation in the shake flask.

7.6 Wet cohesion force of CMC bonded airlaid-hydroentangled fabrics

Having identified that modification of wet fibre-fibre friction is potentially one mechanism by which dispersibility is improved and wet tensile is reduced in CMC containing fabrics, airlaid-hydroentangled fabrics were evaluated using the wet pull out test described in section 3.3.7. Measurement of the wet cohesion force characterises inter-fibre sliding friction in the wet state and could therefore be useful in explaining the wet tensile strength and dispersibility results for fabrics containing CMC. Fabrics were made from 80:20 wood pulp:lyocell 6 mm, 1.7 dtex with an applied specific energy of 6.85 $MJ.kg^{-1}$. For the impregnated fabrics, a 0.025% w/v solution of D.S. 0.55 CMC (Niklacell) was applied using the pad mangle applicator. Printed CMC fabrics were produced using the method described in section 7.2.1 with a 5% w/v solution of Finnfix 700 (D.S. 0.7). These fabrics were evaluated with and without 10% w/v NaCl in the lotion, to determine the effect of salting out on fibre frictional properties. The results of MD wet cohesion force are summarised in Figure 7.13.

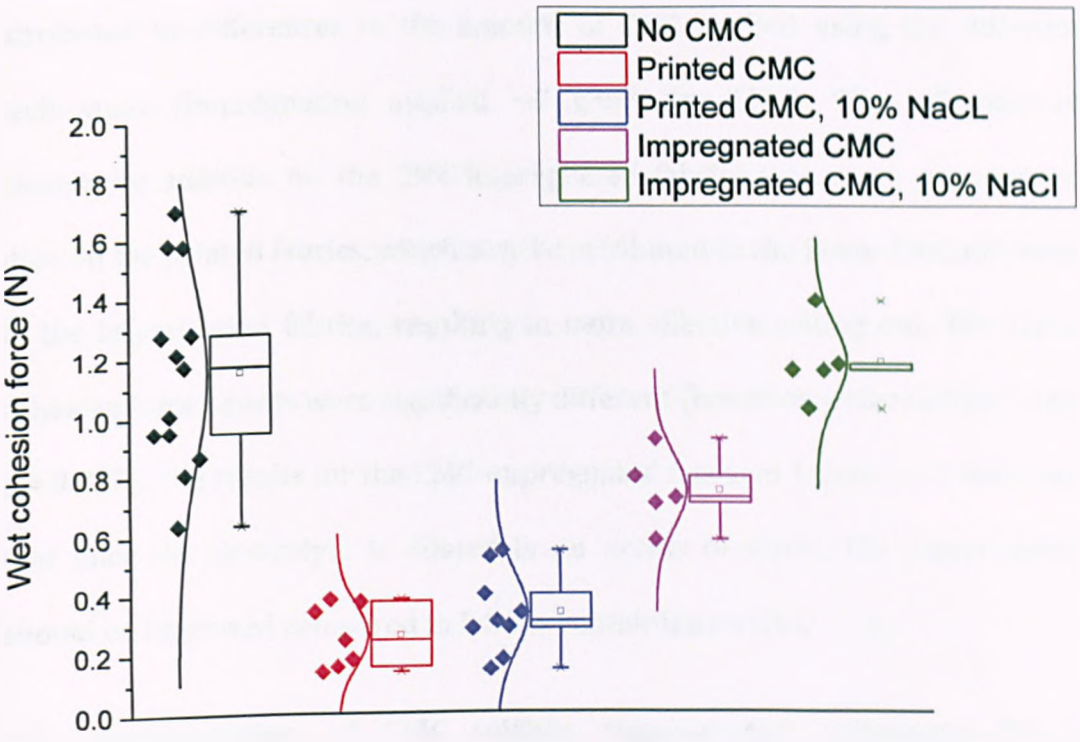


Figure 7.13. MD wet cohesion force of wood pulp-lyocell (6 mm, 1.7 dtex) airlaid-hydroentangled fabrics containing CMC with and without NaCl in the lotion

Printing the fabrics with CMC resulted in a substantial reduction of about 65% in the wet cohesion force compared to the untreated control. This appears to confirm that CMC does reduce inter-fibre frictional force considerably in the fabric, or at least has a lubricative effect. If fibres disentangle more easily then the wet tensile strength will reduce and dispersibility will increase, which is what has been observed experimentally. Adding electrolyte (NaCl) to the lotion did not markedly improve the wet cohesion force of the printed fabrics, which might be anticipated given the high level (~25 $g.m^{-2}$ dry weight of CMC) of addition of CMC on the printed fabric. Impregnating CMC onto the airlaid-hydroentangled fabrics also resulted in a reduction in wet cohesion force but to a lesser extent than the printed fabrics, reducing the force by approximately 35% compared to the control. This difference in cohesion force can be

attributed to differences in the amount of CMC applied using the different techniques (Impregnation applied ~7 $g.m^{-2}$ dry CMC). The influence of electrolyte addition on the CMC-impregnated fabrics was more pronounced than on the printed fabrics, which may be attributed to the lower CMC:salt ratio in the impregnated fabrics, resulting in more effective salting out. The mean cohesive force results were significantly different (based on a two sample t-test, $p = 0.007$). The results for the CMC-impregnated fabric in Figure 7.13 indicated that once the electrolyte is diluted in an excess of water, the dispersibility should be improved compared to fabrics containing no CMC.

7.7 Incorporation of CMC within regenerated cellulosic fibres (viscose and Tencel)

Having established that CMC addition in the form of a binder applied to the fabric reduces the wet tensile strength of mechanically entangled short fibre nonwovens, other methods of incorporating CMC were considered with the aim of studying wet tensile strength and dispersibility. Previously, CMC has been successfully added to the spinning dope of viscose fibres to produce regenerated cellulose fibres with higher absorbent capacity (117, 268). To understand if direct incorporation of CMC in fibres could assist in achieving an effective balance of high wet tensile strength and dispersibility, CMC-doped viscose and CMC-doped lyocell fibres were produced, the latter being based on standard lyocell. Both were supplied by Lenzing AG.

Carboxymethyl cellulose powder (Niklacell T50 G) was dissolved into the viscose and lyocell spinning dopes prior to wet spinning. The CMC addition level was varied between 1-5% by weight. The resulting fibres were cut to 6 mm length before airlaying 80:20 with wood pulp and subsequent hydroentanglement at the same applied specific energy (6.85 $MJ.kg^{-1}$). 10% NaCl was added to the wetting lotion. The wet and dry MD tensile strength of these fabrics is shown in Figure 7.14 and Figure 7.15.

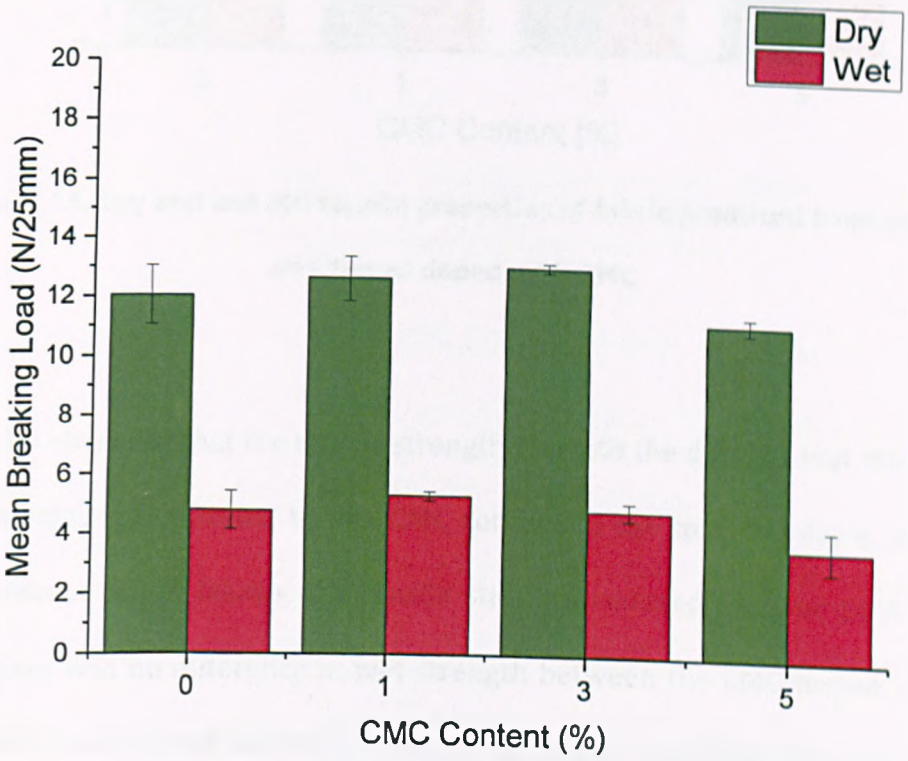


Figure 7.14. Dry and wet MD tensile properties of fabric produced from viscose doped with CMC

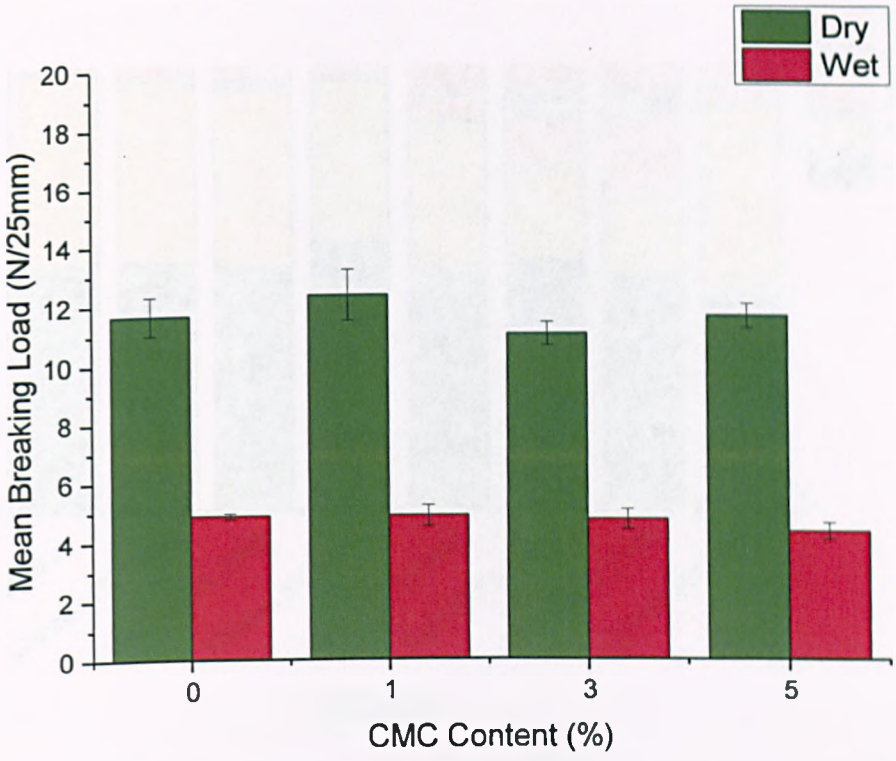


Figure 7.15. Dry and wet MD tensile properties of fabric produced from viscose and Tencel doped with CMC

It may be observed that the tensile strengths in both the dry and wet states are not systematically affected by the CMC content in the spinning dope. As with other viscose-based fabrics, the tensile strength reduced by over 50% when wet. There was no difference in wet strength between the CMC-doped viscose and CMC-doped lyocell fabrics, possibly because the crystalline structure of the lyocell fibre may have been reduced by addition of the CMC. The corresponding influence on dispersibility after 6 hr shake-flask testing is shown in Figure 7.16. Data for non-doped fibre viscose and lyocell samples produced in the same blend proportions and using the same manufacturing conditions are included for reference.

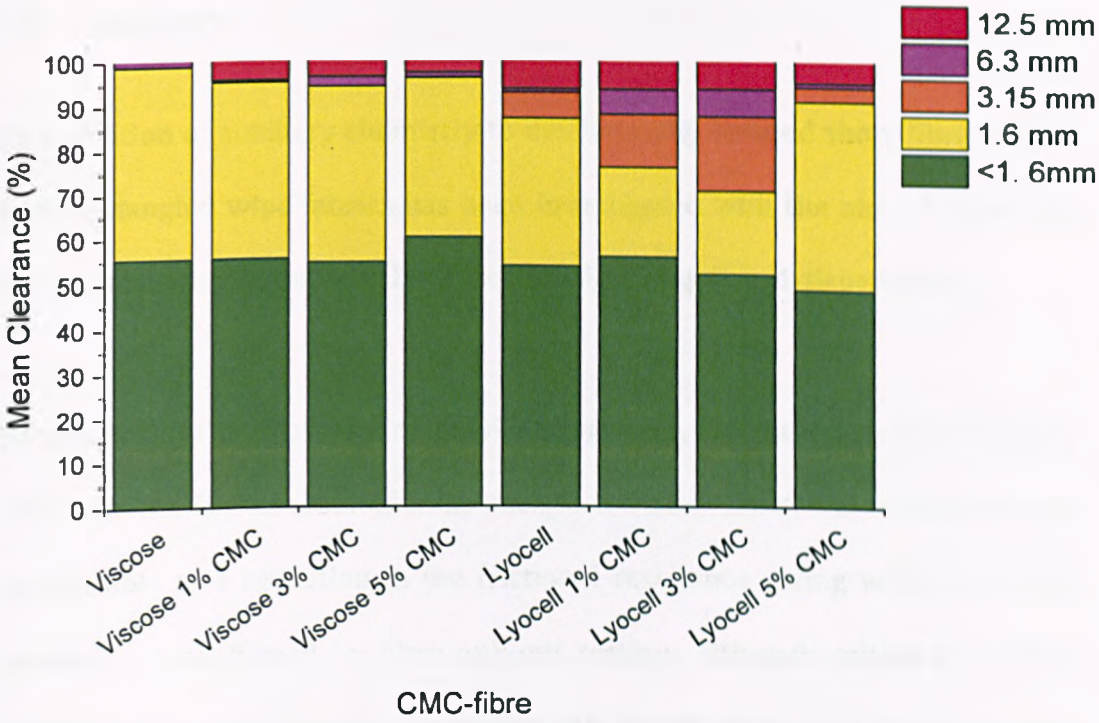


Figure 7.16. Dispersibility properties of fabric produced from blends of woodpulp and viscose or Tencel doped with CMC

The dispersibility of CMC-doped lyocell fabrics reduced compared to the CMC-doped viscose fibre fabrics. This mirrors the difference that has been reported herein between the dispersibilities of fabrics containing viscose and standard lyocell (without CMC doping). In contrast to the application of CMC as a topical coating, incorporation of CMC within the fibres during spinning did not confer improved dispersibility behaviour. This may be indicative of the CMC not being available at the surface of the fibre, but rather being isolated within the surrounding cellulosic polymer matrix of the viscose and lyocell fibres. Under such circumstances it is unlikely that surface friction would be substantially modified, since it is an interfacial mechanism between fibre surfaces.

7.8 Summary

The addition of auxiliary chemistry to mechanically bonded short-fibre airlaid-hydroentangled wipe fabrics has been investigated with the aim of improving the performance, in terms of both wet tensile strength and dispersibility.

Whilst slightly increasing dry tensile properties, printing and impregnating CMC onto the fabrics resulted in an unexpected decrease in wet tensile strength, attributable to a reduction in the frictional resistance acting within the fibre network, as confirmed by fibre pull-out testing. Although salting-out effects could be discerned, it could not compensate for the change in surface friction brought about by coating of the fibre surfaces by CMC. In terms of salting out as a means to promote wet strength in CMC-treated fabrics, the most effective electrolyte was found to be 10% w/v sodium chloride.

The molecular weight of the CMC had little influence on the fabric's wet mechanical strength, whereas reducing the degree of substitution increased the wet strength. Wet strength peaked at pH 5.4, which is appropriate for skin application. Incorporating CMC directly within cellulose fibres prior to extrusion (viscose and standard lyocell) did not yield increases in either wet or dry fabric tensile strength.

CMC addition also influenced dispersibility characteristics. Whilst the CMC improved dispersibility, the disintegration profile was similar despite the method of application or degree of substitution of the CMC. Impregnation of the

CMC on to fabrics, rather than printing resulted in slightly improved and more uniform dispersion probably because it enabled more of the available fibre surfaces to be uniformly coated rather than confining the coating to discrete areas.

Applying CMC to the wipe substrate resulted in a reduction in the wet cohesion force, most likely by reducing the inter-fibre frictional forces. In these conditions, fibres disentangle more readily reducing wet tensile strength and increasing dispersibility.

Addition of electrolyte (NaCl) to the lotion improved the wet cohesion force of fabrics impregnated with CMC. The influence of electrolyte addition to CMC-impregnated fabrics was more pronounced than was observed in the printed fabrics, which may be attributed to the lower CMC:salt ratio in the impregnated fabrics resulting in more effective salting out.

Using CMC's as triggerable binders, whilst attractive to the application, do not impart the strength-dispersion characteristics that are required. Strengths can be maximised through electrolyte addition but the levels required could negatively impact skin health as well as machinery corrosion.

Conclusions

8.1 General Conclusions

Wet wipes are lightweight nonwoven fabrics impregnated with a liquid medium for the purposes of cleaning surfaces. In specific applications such as moist toilet tissue, toddler toilet care wipes, bathroom cleaning wipes incontinence/bathing wipes and feminine hygiene, wet wipes are conveniently disposed of via the sewer network. Accordingly, "flushable" wet-wipe products are now marketed by a number of manufacturers and there has been significant sales growth. As a result, large volumes are being disposed of in domestic toilets, increasing the demands on municipal sewer networks. The resulting impacts on wastewater and sewer systems include sewer blockages, foul odours, sewer flooding, environmental pollution and disruption of pumping station and sewage treatment plant operations. These issues have highlighted the inadequate design of current flushable wipe products.

In Chapter 2, the importance of transportation of flushable wipes through the sewer network was highlighted to ensure satisfactory overall performance. Accordingly, low-medium buoyancy in water, compatibility with household and municipal pumps, biodegradability and rapid dispersibility in water are key criteria. The functional requirements for flushable wet-wipes are somewhat contradictory. A high wet strength is required during use but a low wet strength on disposal is then needed to facilitate break-up sufficient to prevent the wipe being screened out at the wastewater treatment plant. Principally

airlaid and wetlaid processes are preferred to produce wipe fabrics because they can be made from wood pulp and short cut (<20 mm) fibres, which give rise to improved dispersion because of the relative ease by which the fibre assembly can be disintegrated in a hydrodynamic environment compared to longer fibres. Primary mechanisms that have been exploited for the manufacture of flushable wipes can be grouped into three broad categories:

a) Temporary binder systems

b) Binderless systems that seek to achieve flushability via combinations of fabric composition and mechanical bonding

c) Combination of binder and mechanical bonding approaches.

Temporary binder systems that are triggered by a change in the external environment have been a common approach for producing flushable wipes. By the application of a binder whose binding behaviour changes depending on the local environment, mediated for example by pH, ionic strength or temperature, it is possible to obtain both an adequate wet tensile strength and satisfactory dispersibility. However, performance is affected by variations in water composition. Much of the intellectual property focuses on ionic interactions, with electrolyte added to the wetting liquid, which can be affected by divalent ions present in hard water. The technology is relatively expensive and heavily patent protected to prevent competition.

Binderless systems that employ combinations of fabric composition and mechanical bonding, controlled during processing, are also a major focus for flushable wipe technology. The composition of a flushable wipe is critical to its

function. Changing the fibre length, linear density and blend proportion have all been observed to affect wet tensile strength and dispersibility. Mechanical bonding in the form of hydroentanglement has been employed in the most successful binderless systems. The processing conditions, particularly the specific energy, are critical in making the product as strong as possible whilst enabling subsequent dispersibility. Combining such mechanically entangled substrates with a temporary binder could also be employed to maximise wet strength and dispersibility performance.

The experimental study in Chapter 4 sought to extend the understanding of fabric composition and structure and how it relates to wet tensile strength and dispersibility of short fibre nonwovens from wetlaid and airlaid platforms. Analysis of current commercial flushable wet wipe products established the prevalent composition was of cellulose I and II in the form of wood pulp, and short-cut regenerated cellulose fibres, such as viscose or lyocell. Some also contained binders. Substantial disparities in the wet strength and corresponding dispersibility of different wipes were observed. Notably Kandoo toddler wipes, exhibited a wet tensile strength over seven times greater than the other commercially available wipes, but exhibited very poor dispersibility in the standard shake flask test. This wipe was found to be manufactured from a carded web, wherein the mean fibre length was substantially greater than is encountered in airlaid and wetlaid substrates. This highlighted the critical role of fibre length in determining the relative balance of wet strength and dispersibility.

Additionally, analysis of existing commercial wipes highlighted a scarcely reported finding in relation to fibrillation. Fibre residues retrieved from the dispersibility test screens repeatedly showed evidence of fibrillation of lyocell in the commercial wipes containing this particular fibre type. Note that fibrillation was largely absent in the same fabrics prior to placement in the shake flask and so it could be concluded that fibrillation occurs during dispersibility testing.

Also, it might be reasonable to anticipate a roughly linear relationship between wet strength and dispersibility. However, the relationship was more complex. In hydroentangled fabrics, dispersibility was always high, i.e. >90% (>6.3 mm screen) when the wet tensile strength was below a threshold value of approximately 4 N/25mm. Above this threshold value, the relationship was not linear and other parameters such as the mode of fabric bonding, fibre composition and structural architecture played an important role in governing dispersibility.

Following the analysis of commercial wipes in Chapter 4, a systematic study was made in Chapter 5 of the factors affecting both wet strength and dispersibility in experimental wipes manufactured in the laboratory. To maximise practical relevance, these were based on airlaid and wetlaid-hydroentangled substrates, composed of wood pulp and short cut regenerated fibre. In both the airlaid and wetlaid wipes, increasing fibre length from 6 – 10 mm resulted in progressive increases in the wet tensile strength but decreased dispersibility. Increasing the fibre aspect ratio (length divided by the diameter)

increased the wet tensile strength in the both airlaid and wetlaid wipes. However, the rate of increase in the wet tensile strength of wetlaid wipes was greater than for the airlaid samples, suggesting that the optimal aspect ratio may be lower for wetlaid-hydroentangled fabrics compared to airlaid-hydroentangled fabrics. As aspect ratio increased the dispersibility generally decreased particularly when the aspect ratio was greater than 800. Thus, the findings of the current work suggest that the upper limit for aspect ratio is substantially lower than the value of 3000 quoted previously by Tanio et al (136).

Fibre composition of the wipe was found to have a substantial influence on both wet strength and dispersibility, such that in general, higher wet strength fibres yield higher wet strength fabrics. Generally, direct substitution of lyocell, which exhibits higher wet tenacity, for viscose as the regenerated cellulose proportion in blends with wood pulp increased both dry and wet tensile strength of the hydroentangled wipe but the fabrics containing viscose exhibited greater dispersibility compared to those containing lyocell. Increasing the weight proportion of the short cut regenerated cellulose fibre in the blend, whilst reducing the wood pulp content generally led to an increase in both wet and dry tensile strength, confirming the suggestions of Lang and Viazmensky (59, 69). The corresponding influence on dispersibility has not been widely investigated in the previous work and it was interesting to understanding how blend proportions could influence performance. In both the wetlaid and airlaid-hydroentangled wipes the dispersibility of samples containing 20% Tencel A100/80% pulp and 25% Tencel A100/75% pulp was

found to be similar but decreased when the Tencel A100 content increased to 30% (>90% for >12.5mm screen for wetlaid, <90% for >1.6mm screen, for airlaid). This difference was attributed to the increased surface area of Tencel A100 fibre available for mechanical bonding, resulting in greater levels of entanglement, which are subsequently more difficult to reverse in the shake-flask conditions.

Considering the numerical blend proportions, the number of regenerated short cut cellulose fibres per gram was also found to have a non-linear relationship with the wet tensile strength. Essentially, as would be anticipated the wet tensile strength increases by increasing both the fibre length and the proportion of regenerated short cut cellulose fibres in the blend with wood pulp. However, the upper values of each are of course limited by the need to enable dispersibility. Practically, subject to the optimisation of the specific energy applied, it was apparent that in airlaid-hydroentangled fabrics, the upper limits of fibre length and regenerated cellulose short-cut fibre content was 6-8 mm and 30%, respectively to ensure dispersibility of >95% (>12.5mm screen). This compared to 8-10 mm and 20%, respectively in the wetlaid-hydroentangled fabrics, which suggests that the web formation method influences the efficiency of entanglement of fibres during hydroentanglement. These differences were exemplified using X-ray Microtomography in Chapter 5.

As expected the wet strengths of experimental wipes produced in this work were consistently lower than their corresponding dry strength. However, some exceptions were observed, which is noteworthy. Unexpectedly, in some of the

airlaid samples, the wet strength was actually consistently higher than the dry strength, because of differences in the mechanisms of bonding. Dry tensile failure in wetlaid fabrics due to both fibre and hydrogen bond breakage resulted in low strain-high stress behaviour and brittle fracture. For dry-state airlaid fabrics, stick-slip behaviour was observed before tensile failure, consistent with fibre slippage resulting in ductile fracture. In the wet state, both wetlaid and airlaid fabrics exhibited ductile-type stick-slip behaviour with frictional resistance, as a result of fibre entanglement largely responsible for generating tensile stress. During tensile straining of the airlaid-hydroentangled fabric, when the wet frictional resistance exceeds the combination of dry entanglement friction and fibre strength, fabrics with a wet tensile strength which is higher than the dry state can be explained. It is likely that the reason that this counter-intuitive observation has not been previously observed is that current flushable wet wipe production is focused almost entirely on wetlaid substrates.

The same applies for previous research in this area. Based on the findings from the present work, using an airlaid-hydroentangled platform it is possible to produce a wet wipe with a wet strength as high as 22 N/50mm with dispersibility of 100% (<12.5 mm screen). This is highly significant because as indicated in section 2.9, it exceeds the aspirational target recently set by a leading manufacturer for a wipe with a wet tensile strength of 15 N/50 mm and ≥95% dispersibility (12.5 mm screen), measured in accordance with the INDA/EDANA GD3 flushability guidelines. It is therefore apparent that airlaid-

hydroentangled fabrics have greater potential as wet wipe substrates than has been previously recognised.

Specific energy consumed during hydroentangling was found to offer an effective means of controlling the balance of wet strength and dispersibility in both airlaid and wetlaid substrates. Over the range of specific energies studied, linear correlation was observed between wet tensile strength and specific energy, but because of the short length of the constituent fibres and pulp there was an upper limit to the specific energy before excessive fibre displacement and ultimately disintegration of the web occurred. Clearly, fibre entanglement would be anticipated to increase as the specific energy increases, and therefore, as expected, the dispersibility generally reduced with increasing specific energy. Note that there are marked differences between the wetlaid and airlaid-hydroentangled substrates in terms of the specific energy that could be applied. Generally, it was observed the upper limit of specific energy that could be applied to the airlaid substrates was greater than the wetlaid, before the web began to disintegrate. Also, it is doubtful, based on the observations made herein that fibre entanglement in the wetlaid samples increased substantially as a result of increasing specific energy because of the density of the web and relatively immobility of fibre segments. Rather, it is likely that the web is consolidated mainly by compressive forces during hydroentangling, whereas in the airlaid webs there is greater opportunity for fibre end migration due to the lower web density and greater ease by which fibre segments can be displaced.

The hydroentanglement forming belt open area also influenced fabric wet tensile strength. Decreasing the open area of the screen to ≤ 38.5% open area (50 mesh) resulted in less fibre loss during hydroentangling as a result of washing out and increased both the dry and wet fabric tensile strength, probably because of the greater proportion of longer fibres that were left in the structure. Little difference in wet and dry tensile strengths was observed between 31.8-38.4% open area (50-100 mesh). Unexpectedly, screens with the highest open area resulted in the lowest dispersibility possibly due to the passage of pulp and short fibres through the screens during hydroentangling, such that there were localised areas of intensely entangled longer fibres in the resulting fabric, which do not easily disentangle.

The mechanism of dispersion in short-fibre hydroentangled fabrics is not well understood and there is no previous academic research in this area. It was established in the present work that placement of a wipe in excess water alone does not necessary induce dispersibility. Interestingly, no change in wet tensile strength was observed after saturation in water for extended periods up to 6 hr. Furthermore, it was established that the most likely dispersion mechanism in the shake flask is the result of fibre slippage, meaning that wet fibre-to-fibre cohesion and frictional resistance to sliding is critical in governing the break-up of the substrate. With fibres of short length the distances over which they must be displaced before they can be separated is obviously small. Accordingly, once the frictional forces associated with sliding friction can be overcome, the fibre-to-fibre contact points can be completely separated within a very small

distance. To understand the magnitude of the wet cohesive forces involved, a wet pull out test was devised.

The wet cohesive force for samples containing lyocell was higher than in samples containing Tencel A100 and viscose fibre, which suggested that samples containing Tencel A100 or viscose might disperse more readily than those containing standard lyocell. As was expected, the wet cohesion force increased with increasing specific energy during hydroentangling and increasing regenerated cellulose fibre content. Interestingly again with these samples, it was observed that when the wet cohesive force increased, dispersibility in the shake flask was adversely affected. Accordingly, it was apparent that the wet pull out test and specifically, the measurement of wet cohesive force could be a simpler, faster and more reliable method of assessing the dispersibility of wet wipes than using the shake flask. Importantly it negates the effect of fibre fibrillation, which may not be apparent when wipe fabrics disperse after disposal in the sewer network.

Numerical models based on linear multiple regression methods suggested specific energy and the total regenerated fibre length influence the wet tensile strength of the fabrics. However, the total fibre length negatively influences dispersibility. Fibres that are resistant to fibrillation benefit dispersibility. The model for wet tensile strength was found to be in relatively good agreement with the experimental data, but less so for dispersibility. Dispersibility cannot be conveniently expressed as a unitary value based on mean clearance through

a particular screen, which complicates numerical modelling using regression methods.

For the first time, the experimental work in Chapter 6 systematically established the importance of resistance to fibre fibrillation during shake flask testing on corresponding dispersibility. Similar observations were made by Lang (69) on fabrics containing high levels of lyocell but no study has been conducted on fabric compositions including high (>75%) levels of wood pulp and regenerated fibre, which are commonly sold commercially.

Fibre fibrillation was found to have a marked influence on the dispersibility behaviour of both wetlaid and airlaid hydroentangled wipes. Fabrics containing Tencel A100 and viscose exhibited the greatest resistance to fibrillation and consequently produced the highest dispersibility in the shake flask. Despite being produced using a crosslinking procedure designed to reduce fibrillation propensity, substrates containing Tencel A300 and Tencel A300(2) as well as non-cross-linked standard lyocell were found to be susceptible to fibrillation, which consequently reduced their dispersibility. The importance of resistance to fibrillation was further reiterated by the linear relationship obtained between Canadian Standard Freeness after 60 minutes and dispersibility of substrates in the shake flask.

These cast doubt upon the validity of the shake-flask test as a standard method for measuring dispersibility since the test itself may be responsible for inducing a fibre response in the form of fibrillation that is unlikely to occur in practice.

Therefore, fabrics that contain fibres that are susceptible to fibrillation may be unduly penalised in dispersibility testing.

The dispersibility of airlaid and wetlaid fabrics differed, with the wetlaid fabrics showing better dispersion due to differences in structure resulting from the two web forming techniques. Airlaid webs are more open and have a lower density, and as such fibre displacement is less encumbered and can entangle more efficiently during hydroentangling. Conversely, the wetlaid structure is denser, due to the hydraulic force that is applied during fibre deposition. This restricts the degree to which fibre entanglement can be developed in the fabric during hydroentangling with the same applied specific energy. This has not been previously observed by other researchers because of the hitherto limited application of airlaid processes in the manufacture of flushable wet wipes. The potential for airlaid technology in the formation of flushable wipes appears to be high given the significant levels of fibre entanglement that can be developed, whilst not compromising fibre disentanglement during shake flask testing.

For short fibre hydroentangled nonwovens comprised of wood pulp and regenerated cellulose fibres, the fibre properties are critical to their performance. New evidence has been presented here to suggest optimised wet sliding friction and fibrillation resistance are key parameters required to improve the balance of wet strength and dispersibility of the resultant fabrics. There is an opportunity for the introduction of a new cross-linked lyocell fibre with high crystallinity and high fibrillation resistance, as well as appropriate

wet frictional properties, to create high-strength fabrics that be rapidly dispersed after disposal.

8.2 Suggestions for Further Work

The present research has been particularly focused upon the competing requirements of wet strength and dispersibility of short fibre hydroentangled wet wipes. The need for additional study in future work can be identified as follows:

- Frictional properties have been identified in the present work as a critical parameter in both contributing to wet strength and enabling dispersibility. Fibres capable of providing triggerable frictional properties would be a worthwhile area of study, to enable high friction during use and low friction after disposal.
- This work has highlighted a number of important properties, such as total fibre length, dimensions and fibrillation resistance that influence a wipe substrates strength and dispersibility. Further research would benefit from a full factorial study design to understand the relative importance of the main properties.
- Regenerated cellulose fibres with high fibrillation resistance and high modulus could lead to high wet strength wipe fabrics with high levels of dispersibility. Tencel A100 has shown some of this behaviour but the stability of the fibre in acid conditions could make it unsuitable for use in wet wipes. Further research is required to understand the long-term use of cross-linked regenerated cellulose fibres in wet wipe applications.

- Fibrillation has been observed to prevent dispersion during shake-flask dispersibility testing. It is unclear whether such fibrillation would be observed during disposal in the sewer network as conditions are very different. Further work is suggested to observe the effect of fibrillation under these conditions.
- Hydroentanglement screen open area has been shown to influence the both the tensile properties and the dispersibility of airlaid-hydroentangled wipes. Further research is required to understand the mechanism of influence that the entanglement conveyor design has on wipe properties.
- Self-immolative polymers are designed to disassemble into their building blocks once the disassembly process is initiated by a triggering event. Capping the polymer terminal head-group with a specific protecting group generates a polymeric molecule with a trigger (269, 270). The potential for these polymers to trigger dispersibility is very interesting in response to changes in salt, pH or some other external stimulus.
- The tactile and perceived softness of flushable wipes containing short fibres (<15mm) is still considered by many to be inferior to those containing long staple fibre. Whereas the former are based on wetlaid and airlaid webs, the latter use carded webs where the fibres may be >25mm in length. Of course, dispersibility of such long fibres can be expected to be very poor. To address this limitation, it would be valuable to explore methods of constructing wipes from long fibres that have the ability to subsequently reduce in length after disposal.

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